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THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

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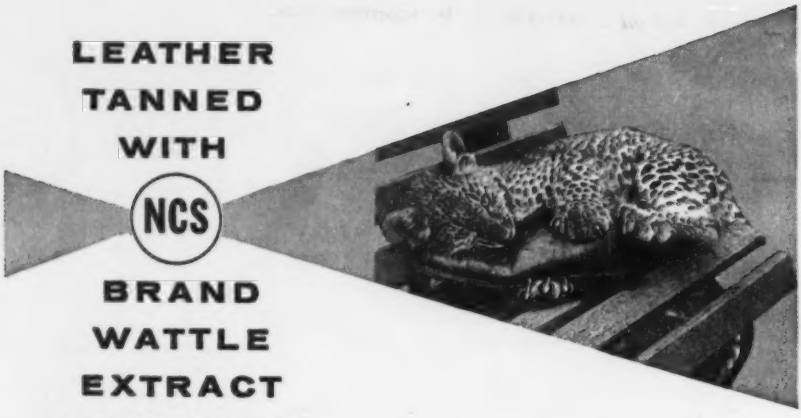

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SECRETARY'S NOTICE

The following notes or changes in methods are for insertion in our Methods Booklet:

Method H-31 "Saponification Value"
Paragraph 4.3—modify to read

"approximately one hour for normal samples."

The following note is to be added:

"Some samples particularly difficult to saponify may require more than one hour. This can only be determined by trial. Clarity and homogeneity of the test solution are partial indicators of complete saponification, but they are not necessarily absolute criteria."

Method H-32 "Iodine Value—Wijs Method"
Paragraph 3.18—add following:

"All Wijs solutions are sensitive to temperature, moisture and light. Store them in a cool and dark place and never allow them to come to a temperature much above 30° C."

Method C-1 "Chromic Oxide"
Paragraph 4.1.1—modify to read

"The nitric acid may be omitted from the oxidizing mixture if organic matter is known to be low or absent."

Note: The Methods Booklets have been sent only to active members. Other members and subscribers may purchase these methods through the Secretary's office for $2.00.

The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LIV JULY 1959 No. 7

CONTENTS

The Shrinkage of Hide—A Melting Phenomenon - - - - - - - *By* L. P. WITNAUER and J. G. FEE 374

A Chrome Alum—Collagen System - *By* K. H. GUSTAVSON 390

Life Lines - - - - - - - - - - - - 399

ALCA News - - - - - - - - - - - - 400

Abstracts - - - - - - - - - - - - 412

Patents - - - - - - - - - - - - - 426

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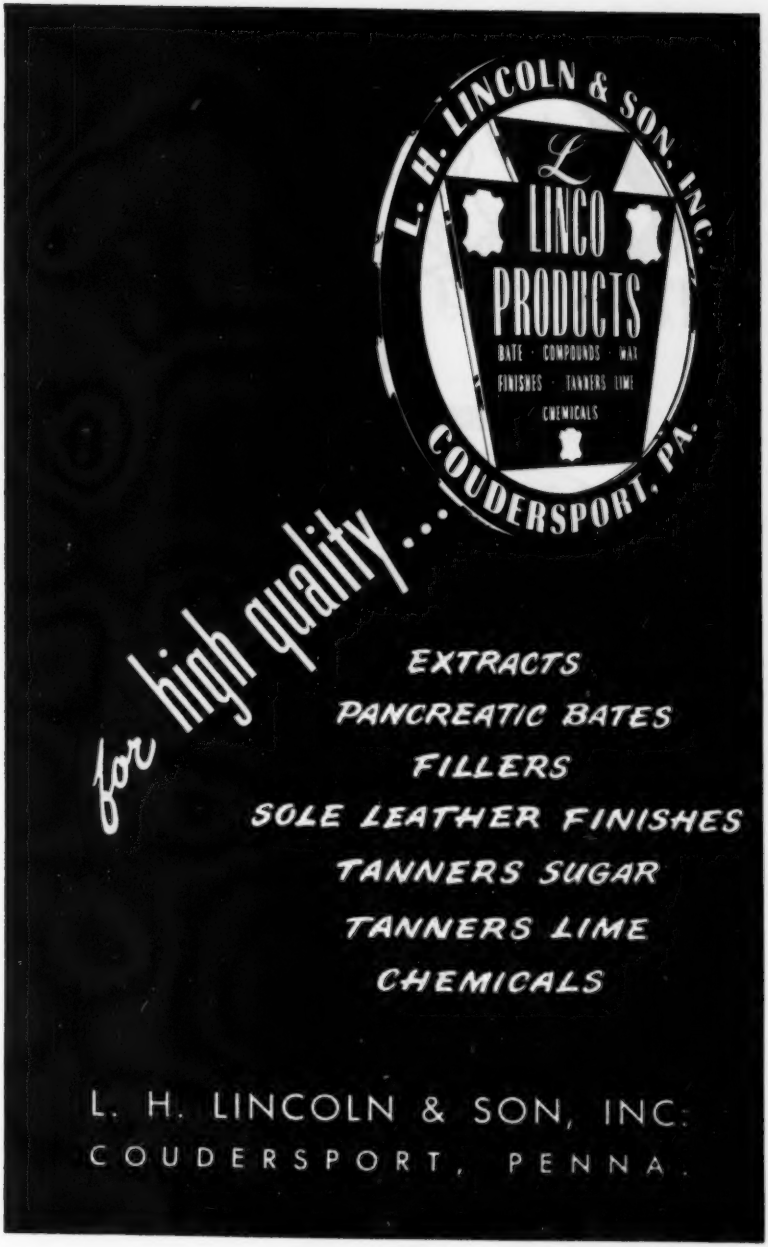
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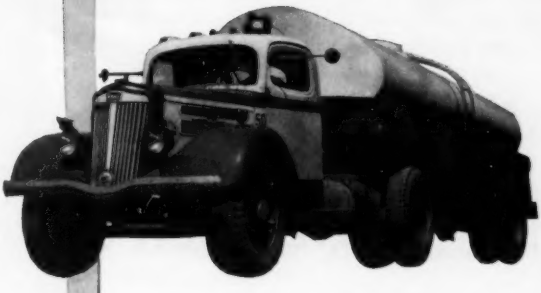

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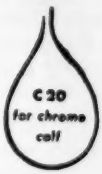

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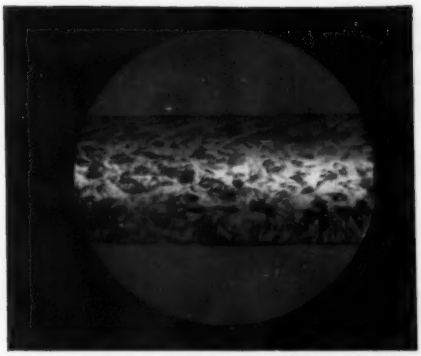

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General correspondence concerning the *Journal* should be mailed to the Managing Editor.
Subscriptions—$12 per year for members; $15 for nonmembers.

THE SHRINKAGE OF HIDE—A MELTING PHENOMENON*

LEE P. WITNAUER AND JEANNE G. FEE

Eastern Regional Research Laboratory†
Philadelphia 18, Pennsylvania

ABSTRACT

The behavior of hide substance when subjected to heat in the presence of small amounts of compatible diluents such as water, ethylene glycol, formamide, and phenol was shown to be analogous to the depression of the melting point of any crystalline substance by a diluent. Various types of tanning agents interact with the polypeptide chains of the hide in different ways, modifying to some extent the ultimate effect of the diluent on the shrinkage temperature. The results from tanned hide specimens indicated that tanning agents reduce the amount of water that can reach the polypeptide chains and, as a consequence, produce the commonly observed elevation in shrinkage temperature.

—✕—✕—

INTRODUCTION

It is well known that hide substance when heated in water or other polar substances undergoes a marked dimensional change, namely shrinkage, at a specific temperature. This behavior has been variously described as due to degradation, denaturation, rearrangement, gelation, or various combinations of each of these processes. Recently Garrett and Flory (1) investigated this transformation and observed that tendon collagen containing ethylene glycol abruptly increased in volume at a specific temperature which depended on the glycol content. Is this behavior unique for collagen? No, it is characteristic of the melting of any semicrystalline polymeric substance; melting is always accompanied by dimensional changes. The melting point of such polymers is always lowered by addition of a diluent. The amount of depression of the melting point is proportional to the amount of diluent present.

This lowering of the melting point is analogous to that of the molar depression of the freezing point of water or other liquid by the addition of a

*Presented at the Fifty-fourth Annual Meeting, Swampscott, Massachusetts, May 26, 1958.
†Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

solute. For example, if a small amount of ethylene glycol were added to finely crushed ice at a temperature well below the freezing point of water and if the temperature were slowly raised, the melting point of the ice would be lowered well below 0° C. The amount of depression would depend on the ratio of the molar quantities of the glycol and water present. It should be pointed out that the diluent in such a system must be compatible (miscible), that is, be able to form a single phase on fusion. The addition of an inert substance, such as a hydrocarbon, to ice would not alter its melting point.

Flory was able to show that the theory of melting-point depression as applied to semicrystalline polymers was also applicable to the collagen–ethylene glycol system (1); thus, the principal event that occurs in the shrinkage of collagen is a melting phenomenon.

The application of the term "melting" to the shrinkage of collagen is not new. As early as 1932 Wohlisch (2) considered the transformation as such a phase transition. More recently Wiederhorn (3) and coworkers discussed the shrinkage of collagen from this point of view. Additional evidence that lends support to this theory is found in other published works. For example, Astbury (4) observed that the characteristic X-ray-diffraction pattern of crystalline collagen disappeared on shrinkage. Theis (5), Kutyanin (6), and Lenox (7) found that the shrinkage temperature depended on dilution.

Although the exact structure of collagen still is not known, much has been learned about it (8). The polypeptide molecules that make up collagen are found to arrange themselves in the form of a regular coil or helix. This helical structure which is stabilized by hydrogen bonds has the properties of a relatively rigid rod. These rodlike particles are aligned in a parallel array forming an ordered phase. One explanation for shrinkage might be that a disordering of this parallel array takes place. Although the amount and strength of the interhelix forces are not known, experimental evidence indicates they may be relatively small. It is well known that unmodified hide swells when immersed in water or other highly polar substances. Doty (8) recently showed that it is possible under the proper conditions to swell collagen to such an extent that the rodlike particles are separated from one another in a medium. This separation of the helices occurs without loss of the helical structure and implies that interchain order may not play a major part in the shrinkage process of unmodified collagen. It would then appear that the shrinkage process could simply be explained by the transformation that takes place within each helix.

Such a process can still be considered a melting phenomenon analogous to that of the melting of an ice crystal that is held together by hydrogen bonds. Whether the rearrangement is a result of a reduction of order between helices or within a helix does not invalidate the application of principles of first-order transition to collagen.

With these considerations in mind, we decided first to investigate whether the melting-point theory was directly applicable to hide substances (9) and then to determine if it were applicable to tanned specimens. The latter investigation might aid in explaining some of the effects of tanning.

EXPERIMENTAL

The hide used was pickled stock obtained from a local tannery. For these experiments it was depickled to pH 4.9, washed in running tap water, and dehydrated in acetone. The vegetable-tanned samples were of commercial upholstery leather which was analyzed for total hide substance by determination of nitrogen. The formaldehyde tanning was carried out in a 1% formaldehyde, 0.1 molar sodium bicarbonate solution to a final pH of 7.5. The leather was then washed free of unreacted tanning agent and air-dried. The dialdehyde starch tanning (10) for all except one sample was carried out with 33, 66, or 96% oxidized dialdehyde starch in a mixed buffer solution at pH 9.8. The exception, a sample tanned with 96% oxidized dialdehyde starch, was tanned in a straight sodium bicarbonate buffer solution at pH 8.8. The samples were subsequently washed in running water and air-dried.

Specimens for the shrinkage measurements were cut from these samples in strips 2.5″ long, 0.25″ wide, and about 0.15″ thick. The specimens were subsequently dried under vacuum at 50° C. Approximately seven hours was required for the sample to attain constant weight. The dried specimens were equilibrated in an evacuated desiccator over the diluent in the cases of ethylene glycol and water. The glycol-containing desiccator was heated to 60° C. to facilitate attainment of equilibrium, which required as long as six days in some cases. Although water vapor was quickly absorbed by the hide specimens at room temperature and 100% relative humidity, water contents of above 40% (based on total weight of specimen plus water) could not be obtained by this technique. For the higher water contents, the specimens were soaked three minutes in distilled water and then allowed to dry slowly in an atmosphere of 100% relative humidity until the desired water content was attained. In preparing samples of varying phenol or formamide content, it was necessary to soak the dry hide samples in absolute alcohol solutions of phenol or formamide. Varying amounts of these diluents were obtained in the specimens by changing the concentration or time of soaking. After soaking, the samples were conditioned in a vacuum desiccator containing desiccant for at least 24 hours. The diluent content of the cowhide samples reported here is based on total weight of sample and diluent.

The instrument used in measuring the shrinkage temperatures of the samples has been described in a previous paper (11) and simply provides a means of measuring changes in length with an accuracy of ±0.001″. In determining the shrinkage temperature a sample of known diluent content was immersed in a mercury bath to prevent loss of diluent during the test.

The mercury bath was surrounded by a glycol bath in which the heater and stirrer were immersed. The temperature was measured by placing a thermometer in the mercury bath. As a result of numerous trial runs the following rate of heating was chosen as most suitable and expedient. The sample was heated at a rate of 3° C. per minute up to approximately 10° C. below the expected shrinkage temperature (on the basis of a trial run). The rate of heating was then decreased to ½° C. per minute through the shrinkage range. The shrinkage temperature was considered to be that at which a sharp change in slope occurred in the temperature versus length plot. This temperature was reproducible to ±1° C. in separate runs.

RESULTS AND DISCUSSION

In order to determine whether shrinkage is associated with a melting phenomenon in hide substance, the apparent melting (shrinkage) temperatures of unmodified hide specimens containing varying amounts of ethylene glycol were measured. The results are shown in Fig. 1 along with the data

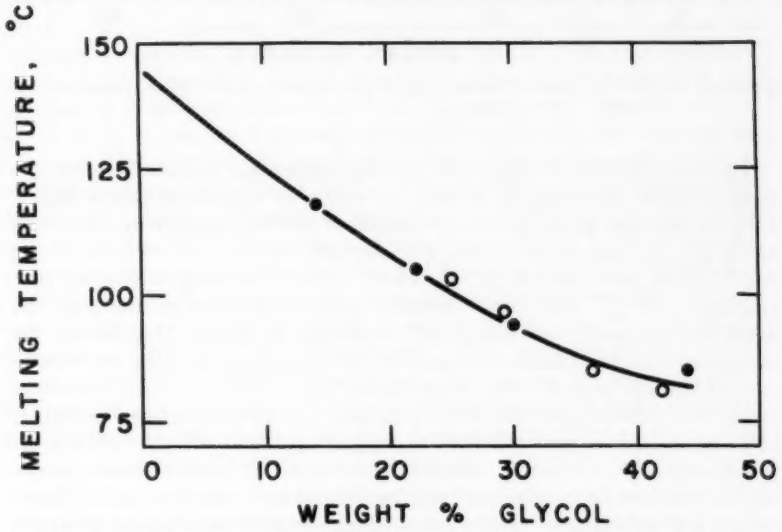

FIGURE 1.—Plot of apparent melting (shrinkage) temperature of hide vs. weight percent glycol. Dilatometric melting-point data of Garrett and Flory (●); data obtained by shrinkage measurements (○).

reported by Garrett and Flory (1) for ethylene glycol–tendon obtained using a dilatometer. The agreement between the two sets of data is remarkable considering the fact that both the origin and treatment of the samples studied were quite different.

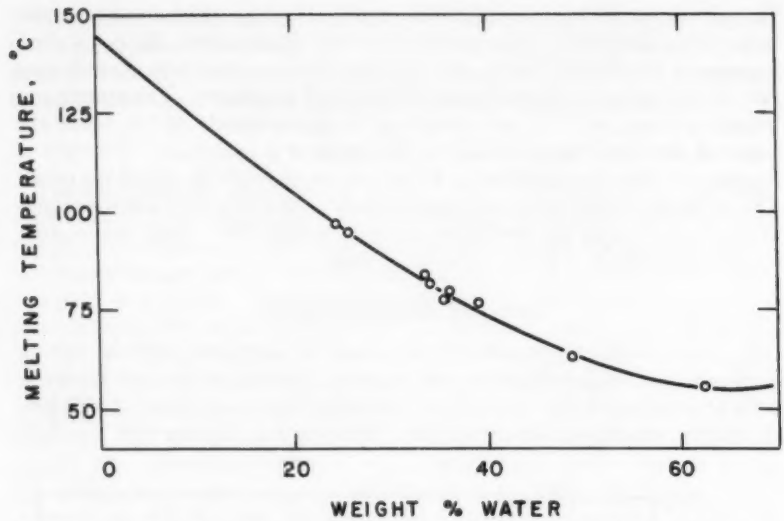

FIGURE 2.—Plot of apparent melting (shrinkage) temperature of hide vs. weight percent water.

The variation in the apparent melting (shrinkage) temperature for unmodified hide containing 25 to 62% by weight of water is shown in Fig. 2. Like the ethylene glycol system, the apparent melting temperature decreased as the diluent content increased. For example, the hide specimen containing 24.5% water contracted at 97° C., while the one containing 62% water contracted at 56° C. The latter temperature was the same as that obtained when the specimen was completely immersed in water. Apparently the maximum amount of water that is effective in lowering the melting temperature of the polypeptide helix of bovine collagen is about 62%. Specimens taken from different portions of the same hide and from other hides (including calfskin) in general gave the same melting temperature (56° C.) when completely solvated with water. The temperature 56° C. is therefore the fundamental characteristic apparent melting (shrinkage) temperature of limed bovine hide substances. The corresponding temperature obtained on specimens of unlimed fresh hide (immersed in water) is about 4° higher or 60° C. This value is still below the value, 65° C., reported throughout the literature for untreated hide. However, the heating rates generally employed are much larger, about 3° to 5° per minute, than those employed in the present work, 1° per minute. In addition, the instruments usually employed do not permit detection of extremely small changes in length as was possible in the present case (11).

If the melting (shrinkage) of hide substance is an outward manifestation of uncoiling of protein molecule or molecules, then the temperature at which shrinkage takes place should be very nearly that observed for the breakup of collagen helices suspended in aqueous solutions. Recently Doty and Nishihara (12) reported the temperature at which the structure of intact collagen helices isolated from calfskins disappeared. For the calfskin collagen helix this temperature was 37° C. and was denoted as a denaturation temperature, as distinct from the thermal shrinkage temperature. This temperature is 23° lower than observed in our study on untreated fresh hide. They presumed the difference between the so-called denaturation temperature and thermal shrinkage temperature to be a measure of crystal energy of the collagen fiber. Careful consideration of their data, however, showed that the so-called denaturation temperature was obtained on calfskin collagen helices which were suspended in a citrate buffer medium (pH 3.7), while the thermal shrinkage temperature used for comparison was measured in distilled water.

It is well known that the shrinkage temperature of hide substance varies with the pH of the solution (13). Therefore, it was thought that the large difference, 23° C., between the reported denaturation temperature and the shrinkage temperature might be due in part to this fact. We then measured the shrinkage temperature of fresh hide substance in citrate buffer (pH 3.7) and found a shrinkage temperature of 40° C., much lower than the value of 60° C. found in distilled water and only 4° C. higher than the reported denaturation temperature. (Hide which had been previously limed shrank at a slightly higher temperature, 43° C., in citrate buffer.) Thus it appears that there is only a slight difference in temperature between the two. It is not unexpected that the hide substance gave a slightly higher apparent melting (shrinkage) temperature than that observed for collagen helices suspended in solution. Flory and coworkers (14) have recently shown thermodynamically that the apparent melting (shrinkage) temperature may be 5° to 10° higher than the equilibrium melting temperature. Thus, we have referred to our values as *apparent* melting temperatures. It appears, therefore, that the shrinkage of intact hide substance is a melting phenomenon and an outward manifestation of the collapse of the helical structure of collagen.

Two other diluents which were investigated with hide substance were phenol and formamide. The results are shown in Fig. 3. The formamide-hide data are represented by the lower curve, the phenol-hide data by the upper curve. Like ethylene glycol and water systems, these show a decrease in the melting temperature with increase in diluent concentration. Although the melting temperatures for the four systems investigated show the same dependence on the diluent concentration, the individual values obtained at the same diluent concentration (weight percent) are different. It should be emphasized that the diluents employed must be able to associate in some manner with the polypeptide chain or chains. They must contain a group

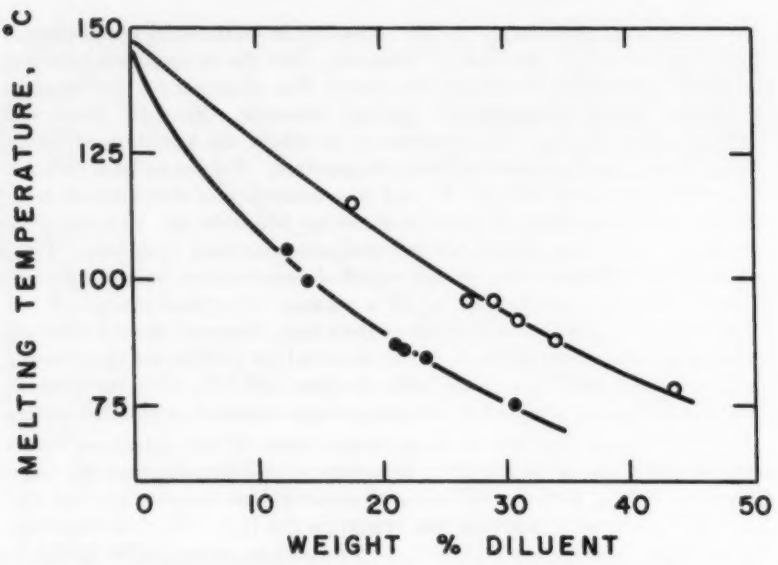

FIGURE 3.—Plot of apparent melting (shrinkage) temperature of hide vs. weight percent formamide (●); phenol (○).

or groups that can interact with a group or groups contained on or within the collagen molecule. For example, phenol is able to act as a diluent, while toluene is completely inert. Extrapolation of the melting (shrinkage) temperature to zero diluent content for all the above-mentioned diluents yielded a value of 145° C. for the theoretical melting temperature of vacuum-dried bovine collagen. Vacuum-dried unmodified hide showed no appreciable contraction even at temperatures up to 150° C.

These results indicate that the shrinkage temperature can be elevated quite simply by limiting the amount of diluent that can solvate (associate with) the helical polypeptide coils. One of the well-known effects that a tanning agent has on hide substance is to elevate the shrinkage temperature as measured immersed in water or other diluent systems. Thus, a tanning agent might be considered as a substance that reduces the availability of the polypeptide chains to the shrinkage medium. This will, in general, be true regardless of the types of tanning agents employed. It should be emphasized again that the tanning agent must itself become associated with the polypeptide, either through hydrogen bonds, covalent bonds, or electrostatic bonds. A completely unassociated hydrophobic material incorporated in unmodified hide substance would only exude out or sweat out, and any blocking action toward a diluent would be of very short duration.

A preliminary investigation of the melting-point depression in hide specimens that had been tanned with a vegetable tannin, formaldehyde, and dialdehyde starch was undertaken. Water was the diluent used. Like the untanned hide, the shrinkage temperature of the tanned specimens decreased with increasing water content. Diluents other than water would be expected to exhibit a similar behavior.

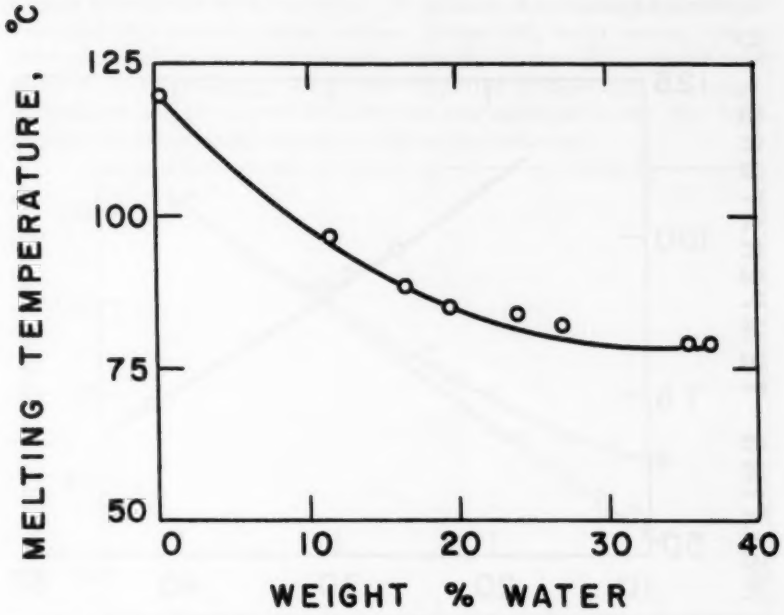

FIGURE 4.—Plot of apparent melting (shrinkage) temperature of vegetable-tanned hide vs. weight percent water.

Shown in Fig. 4 are the data obtained on vegetable-tanned samples of commercial upholstery leather. The shrinkage temperatures ranged from 97° C. with 11.5% water to 79° C. with 37% water. The shrinkage temperatures of vegetable-tanned hide specimens at low water contents are lower than those found for the unmodified hide–water system. For example, a tanned specimen containing 25% water was 13° lower than that of unmodified hide of similar water content. When specimens were immersed in water, these shrinkage temperatures were reversed: the vegetable-tanned specimens shrank 22° higher. The reason for this reversal might be that vegetable tannin itself could act as a diluent, probably because of a loose association of its polar groups with the polypeptide chains. This diluent action of

vegetable tannin was verified experimentally. It was found that vacuum-dried vegetable-tanned hide on heating underwent an unmistakable shrinkage at about 120° C. The shrinkage temperature was not nearly as well defined or reproducible as the other shrinkage measurements. It appeared to have occurred over a temperature range, indicating that in the tanned specimens used, the tanning agent was not distributed uniformly throughout the hide substance.

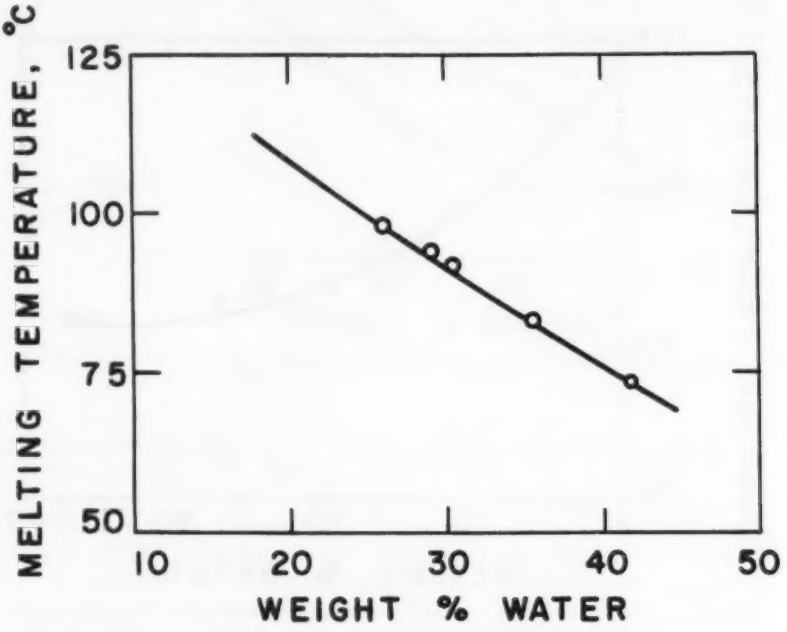

FIGURE 5.—Plot of apparent melting (shrinkage) temperature of formaldehyde-tanned hide vs. weight percent water.

Shown in Fig. 5 are similar data for formaldehyde-tanned hide. The melting temperatures ranged from 90° C. for a specimen containing 26% water to 73° for 40% water. When immersed in water, its shrinkage temperature was also 73° C. The effective water content of the immersed formaldehyde-tanned hide was about 23% less than that obtained with unmodified hide. Dry formaldehyde-tanned specimens of hide, when heated at temperatures as high as 170° C., showed no appreciable shrinkage. This behavior was quite unlike that of the vegetable-tanned samples. Apparently the mode of attachment of the formaldehyde to the polypeptide chains is different from that of vegetable tannin. This is not unexpected, as formalde-

hyde is known to form covalent cross links. Since such cross links are relatively short and fixed compared with those of a vegetable tannin, the formaldehyde cannot act as a diluent.

Figure 6 shows the variation in melting temperature with water content for various types of the new tanning agent, dialdehyde starch (10), that has been under investigation at our laboratories. Starches subjected to different degrees of oxidation were employed. In all cases the shrinkage temperature decreased with increased water content. Below 25% water content, the dialdehyde starch specimens all showed essentially the same shrinkage behavior; above 25%, the shrinkage temperature appeared to depend on the amount of oxidation and the type of medium that was employed to tan the hides. Further investigation is required to explain this behavior.

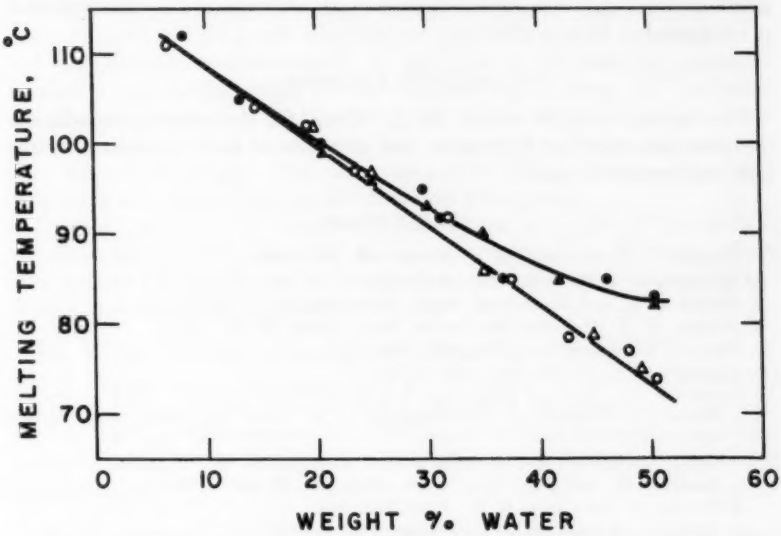

FIGURE 6.—Plot of apparent melting (shrinkage) temperature of hide tanned with 96% oxidized dialdehyde starch, mixed buffer (●); 96% oxidized dialdehyde starch, straight buffer (○); 66% oxidized dialdehyde, mixed buffer starch, (▲); and 33% oxidized dialdehyde starch, mixed buffer (△) vs. weight percent water.

CONCLUSION

The behavior of untanned hide substance when subjected to heat in the presence of small amounts of compatible diluents such as water, ethylene glycol, formamide, and phenol was shown to be analogous to the depression of the melting point of any crystalline substance by a diluent. The temperature at which shrinkage takes place is a fundamental characteristic of bovine

collagen but is dependent on previous treatment. Fresh hide, when heated in citrate buffer at pH 3.7, shrank at 40° C., only 4° C. higher than that observed by Doty *et al.* (12) for collagen helices dispersed in the same medium. This indicated that the macroscopic shrinkage of hide was an outward manifestation of the melting of the collagen helices.

The results obtained from tanned hide indicated that tanning agents reduce the amount of water that can reach the polypeptide chains, which results in an elevation of the commonly measured shrinkage temperature. Various types of tanning agents interact with the polypeptide chains in different ways, modifying to some extent the ultimate effect of the diluent on the shrinkage temperature. Although the discussion presented here has been restricted to the effects of tanning on the shrinkage temperature, the importance of its role in producing the mechanical and other properties desired in quality leather is recognized.

ACKNOWLEDGMENT

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DISCUSSION

PRESIDENT THORSTENSEN: I want to thank Dr. Witnauer for this very fine paper.

My first introduction to this subject was in 1946 when Dr. Theis gave a dissertation on swelling and shrinking before the Faraday Society in London. I never realized at that time what a terrific subject it was and what an honor it was for Dr. Theis to be asked to address that very august body.

Now, in order that we might clarify some of these things, I will ask Dr. Stubbings to come up here and lead the discussion.

DR. ROBERT STUBBINGS (Division of Leather Technology, Lehigh University): We would like to thank Dr. Witnauer for presenting this paper to us on shrinkage. It certainly is an area of shrinkage which I do not think many of us have considered—the area between fully soaked and dry hide.

I was particularly interested in the reduction of shrinkage for untanned specimens between the area of the wet state and the dry state. We had never thought about it much in our laboratory, and yet we knew that dry specimens certainly could be taken to extremely high temperatures, almost to decomposition, without shrinkage. This fills in an area of data, I think, and explains in a much more logical fashion the shrinkage phenomenon.

I would like to ask Dr. Witnauer, before we ask for general questions from the floor, how he feels about the rate process approach to shrinkage which was presented by the Bureau of Standards about five or six years ago by Dr. Weir. Would you like to comment on that?

DR. WITNAUER: All melting phenomena are rate processes. The rate at which melting takes place depends on the particular temperature employed. This is not only true for collagen or semicrystalline polymers; it is also characteristic of crystalline materials. The rate of melting becomes increasingly slower the further the temperature (selected) is below the normally observed melting point.

DR. STUBBINGS: Dr. Witnauer talked about single-intact helices being able to be separated by swelling phenomena and yet retain their helical structure without shrinkage. Dr. Highberger has done work in this field for several years. Will he comment? Can we get single helices?

DR. JOHN H. HIGHBERGER (United Shoe Machinery Corporation, Beverly, Massachusetts): The collagen structure is not a single helix. It is a triple helix. I don't know what the effect would be on what you are talking about. I wondered about that, myself. Does it have any effect?

DR. WITNAUER: No, the melting phenomenon described is generally applicable even if the exact nature of the melting process is unknown. Doty

measured the size, shape, and weight of collagen that was obtained by extraction of carp swim bladder tunics. It was found that the extract consisted of rigid rod-shaped particles or coils. On heating, these coils broke down into three separate molecules. Over-all molecular weight of the new particles formed was slightly greater than one-third that of the original particles. This indicated that the three particles that make up the single coil do not have the same amino acid composition.

DR. HIGHBERGER: I might add that after Doty had gone through that, it was also done with calfskin and codskin collagen.

The Gustavson rule is followed in this particular case, in that the hydroxyproline content of each of these collagens is different, the highest content being at the highest massive shrinkage temperature and the highest denaturation temperature, and the lowest content at the lowest massive shrinkage temperature and the lowest denaturation temperature of the soluble collagen.

There are two possibilities in the structure for the collagen molecule, which are called structures 1 and 2. In one of these, the hydroxyproline bonds are on the outside, and in the other case they are on the inside and take part in holding the three chains together.

Doty believes his work indicates that the latter case is the correct one, although the crystal structure people believe that the first possibility is correct.

DR. WITNAUER: Flory at Cornell University has recently shown that highly oriented rubber undergoes a shrinkage or melting which closely resembles the shrinkage of collagen. The temperature at which melting of the crystallites takes place was found to increase with the amount of tension that the chains have on them. Thus, the observed shrinkage temperature of intact hide substance might be expected to be slightly higher than the equilibrium melting temperature.

DR. HIGHBERGER: That is true, but I would like to point out that the amount of stretch possible in the collagen helix is very small, as you know.

DR. WITNAUER: I meant to imply that as laid down by nature in the fibril, it is under tension.

DR. STUBBINGS: This discussion in terms of the Doty three-helix model, of course, leads to some interesting questions for Dr. Witnauer and perhaps Dr. Highberger.

Following out this method that Dr. Witnauer has shown us this morning, in the region from soaking wet to perfectly dry specimens, it would seem that maybe they could get at some of this internal helix bonding as against bonding between helices by some ionic studies in this area.

Dr. Witnauer has used hydrogen bonding agents as his diluents to study the phenomenon. I am wondering if he has also used any ionic agents which

would tend to disrupt or mask ionic charges perhaps between helices, to see if the breakup then occurs at different temperatures.

DR. WITNAUER: No, we haven't studied ionic systems. I don't know whether you are referring to chrome tanning or not. If you are, our data on this system have not been reproducible. The temperatures required to produce shrinkage in chrome-tanned specimens were 100°C. and higher. At these temperatures bubbling was observed in our immersion medium, and we didn't know whether air or water or water vapor was being driven out of the specimens.

DR. STUBBINGS: I was not specifically referring to chrome tannage, although that too is an interesting phase. I was thinking of salt solutions which would tend to mask the ionic charges but not disrupt the hydrogen-bonded type of structure, to see if there was a difference between the two.

DR. WITNAUER: This is a good point. We have made no investigations along this line.

DR. J. R. KANAGY (National Bureau of Standards, Leather Section): If I understood you right, I believe your work indicates that when you tan with vegetable tanning material, you actually are starting to break down the structure which would be expected with a large molecule. It actually tends to separate the lattices.

Now, the postulation has always been made that in chrome tanning you get cross links. Does your theory still include the fact that you get cross-linking when you have chrome tanning?

DR. WITNAUER: No, vegetable tannins do not appear to break down structure. X-ray studies do not show any effect of the tannin on structure. The only feature that X-ray studies have demonstrated so far is that small molecules, like water, can get between the helices and produce a change in certain lattice dimensions. I don't know whether I have answered your question.

DR. KANAGY: Well, it appears to me from one of the curves you showed in vegetable tanning that when you extrapolated, you had a lower shrinkage temperature than if you extrapolated the curve for the hide.

DR. WITNAUER: Yes, this is due to the fact that vegetable tannin can act in a manner similar to that of water. In other words, the vegetable tannin itself acts as a diluent because of its loose association with the polypeptide chain, just as water or phenol does. Formaldehyde cannot.

DR. KANAGY: I thought possibly the large vegetable tannin molecules might get into the lattices and separate the polypeptide chains. That, of course,

would begin the shrinkage phenomenon, and for that reason you would get a lower shrinkage temperature for tanned hide than for the original hide.

DR. WITNAUER: We tried to take unmodified hide and introduce 10, 20, 30, 40, and 50% of vegetable tannin in it and then apply this theory to it. Because, if it acted as a diluent, then it must obey the theory of melting point depression, just as water did. We were unable to prepare suitable specimens.

DR. ROBERT M. LOLLAR (Tanners' Council Research Laboratory, University of Cincinnati): Did you consider using quebracho in acetone to get known levels of tannin, as Gustavson has done?

DR. WITNAUER: That is the procedure we tried to follow, but we were unsuccessful.

DR. HIGHBERGER: I would just like to point out that with the newer knowledge of collagen structure we know a great deal more than we ever did before about exactly where these cross links do take place in connection with chrome tanning and other types. They take place between groups of three chains and not, as postulated many times before, between individual chains.

DR. PETER R. BUECHLER (Rohm & Haas Company, Philadelphia, Pa.): You have expressed your results here on rate percent of diluent which is added. Have you tried calculating some of these diluents on a molar basis? Does one mole of one material lower the shrinkage temperature as much as one mole of another?

DR. WITNAUER: I did not go into that. If the reciprocal of the shrinkage temperature is plotted against volume fraction of diluent for unmodified hide and the curve extrapolated to zero concentration, the melting point of pure collagen should be obtained. The melting point should be independent of diluent. The same temperature was found for the four diluents investigated. In general the application of thermodynamic equilibrium to phase transitions in the hide systems was satisfactory.

DR. STUBBINGS: In concluding the discussion I would like to say that this approach to tanning by shrinkage of hide in the range from wet to dry might be an interesting way to get at things we have been arguing for years—differences between cross-linked tannage, and materials which we know don't cross-link but which we also know raise the shrinkage temperature in the normal accepted sense of shrinkage temperature.

This business of blocking the sites so that the diluent or solvent medium cannot reach the necessary places may be the answer to a lot of the tannages that have been very vaguely described in the past. I hope this work will be continued at the Eastern Regional Laboratories in this general area.

MR. SALAMATOV: I am interested in what would happen to the structure of the collagen when you remove water completely. That is, to have zero content of water in the molecule. Then electrolytic forces will be dead. Then where and how will the components of the collagen be held together without the electrolytic forces? Is it going to be an amorphous entity, or does it decompose, or what happens to the structure?

DR. WITNAUER: Specimens that were vacuum-dried (constant weight) and studied by X-ray defraction still showed a crystalline type of pattern. The hydrogen bonds in this system are so strong that decomposition takes place before melting. Many other simpler systems on heating will not melt if they are strongly hydrogen-bonded. They decompose.

The outcome of competition with Russia will not depend merely on the race to produce weapons of greater and more instantaneous destructive power, although we must indeed, for our security, strive mightily to excel in this field. It will not depend essentially upon an economic struggle, seeking to win adherence of backward peoples by catering to their needs, and seeking to isolate us in world trade. It will depend, in the last analysis, upon the attitude of our people, and especially of our young men—whether they can face resolutely the threat and the challenge, whether they will strive to excel, vigorously, untiringly, skillfully. In particular, it depends upon whether our youth who are gifted with intellectual talent will develop it to the utmost, with the respect and approbation of their fellows.

—Vannevar Bush.

The first chrome tanning process was patented by Augustus Schultz of New York City. He was granted patents No. 291,784, and No. 291,785 for "tawing" hides and skins on January 8, 1884.

The first belting sold to manufacturers is recorded in the account books of Pliny Jewell, a leather dealer of Hartford, Conn. There is an entry in 1826 of the sale of a leather belt three inches wide. Manufacturers who required belting usually bought skins, cut them to the desired thickness, and by nailing the ends of the pieces to the floor when wet, and driving wedges between the leather and floor, half-way between the ends, stretched them taut.

—*Famous First Facts*, Joseph Nathan Kane, The H. W. Wilson Company, New York, 1950.

In the Boston Art Museum there is a beautiful coat of white antelope that was made in Egypt some five thousand years ago.

The mere formulation of a problem is far more often essential than its solution, which may be merely a matter of mathematical or experimental skill. To raise new questions, new possibilities, to regard old problems from a new angle requires creative imagination and marks real advances in science.

—Albert Einstein

A CHROME ALUM—COLLAGEN SYSTEM

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ABSTRACT

A novel type of tannage with chrome alum is described, in which the acid-binding faculty of the collagen is utilized for the formation of basic chromium sulfate *in situ*. Adhering to a definite proportion of pelt and chromium, chrome alum powder is applied to the pressed pelt. The pelt's moisture dissolves the chrome alum, and the tanning takes place entirely in the skin. After drumming and aging, the chromed pelt is thoroughly washed. The final result is a fully tanned leather which is practically "boil-proof". An outline of the probable reaction mechanism is given.

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INTRODUCTION

In the conventional one-bath chrome tannage, in which the ratio of the volume of the tanning bath to the weight of the hide substance is large, chrome alum and normal chromic salts generally, such as sulfate, chloride, perchlorate, and nitrate, are not satisfactory tanning agents *per se*. The reason for their failure is that the protolysis of these compounds even in dilute aqueous solution does not proceed far enough to form a sufficient amount of the dinuclear basic compounds, such as the $(Cr_2(OH)_2SO_4)^{2+}$ cations, in the instance of chromium sulfates. The formation of such compounds in sufficient amounts is a requisite for the tanning faculty of cationic chromium compounds (1). Moreover, by the protolysis of solutions of normal chromic salts, the pH values tend to be low, which in turn implies a reduction of the number of ionic carboxyl groups in the protein available for the binding of the cationic chromium complexes. Hence, for practical purposes basic chromium salts are usually employed as tanning agents, for instance, by making the 67% acid sulfate from a stock solution of chrome alum by the addition of two moles of sodium hydroxide on each mole of chrome alum.

In the present note, attention will be called to a modified chrome tannage with chrome alum *per se*, without any addition of alkali to the tanning bath. The essential feature of the method is to apply solid chrome alum directly to the moist pelt under specified conditions in order to secure the removal of the protolyzed acid by the collagen and to yield a basic chromium sulfate of suitable basicity in the fiber, and with an amount of chromium sufficient

for securing a complete tannage. It is possible to obtain a moderate tanning effect by chrome alum in the conventional method of chrome tanning by using concentrated solutions. By increasing the concentration of such chromium sulfates, which contain at least one mole of sulfate of alkali metals on each mole of Cr_2O_3, the percentage of acidity of the chrome-collagen compounds formed (chrome leather) is markedly increased, as has been known for a long time (2). The formation of noncationic chromium complexes enters in tanning with solutions of high concentration of such chrome liquors of the sulfate type (2). They contribute to the high percentage of acidity of the chrome-collagen compounds formed (2).

The "dry chrome tanning" which was introduced by Schorlemmer in 1922 (3) is an example of such a tannage. It was conceived from merely practical considerations, at first hand, of the economy in time and tanning agent. The mechanism of the dry tannage was not mentioned at all by Schorlemmer. In this mode of tannage, a large amount of chromium complexes are incorporated with the skin. A part of the same is present in a state of somewhat lower protolytic stability than that of the conventional cationic chrome tanning agents. By washing the leather, which is usually piled up after the tannage in a "short" bath of high chrome concentration, the induced protolysis of the fixed chromium compounds results in the formation of cationic complexes of the type $(Cr_2(OH)_2SO_4)^{2+}$, which impart an additional tanning effect to the leather. These complex changes can easily be ascertained by recording the difference in shrinkage temperature of the original chrome leather by the "shocking" method (4) and the conventional technique of Ts determination. In the dry tannage, chrome liquors of highly basic chromium sulfates, with acidities of 40–50%, can be and are usually employed, since the basic chromium sulfates of the degrees of acidity mentioned are stable at the high chrome concentrations employed, whereby the tanning effect is increased also. The neutral sulfate plays an important role in concentrated solutions of chromium sulfates because it is instrumental in forming anionic compounds of the general type $Na_2(Cr_2(OH)_2(SO_4)_3)$. A most striking and simple proof of the formation of such anionic complexes is the removal of the sulfate ions of the sodium sulfate occurring in highly concentrated solutions of chromium sulfates. This is proved by the fact that sodium sulfate does not crystallize out from such solutions, even if the concentration of the sodium sulfate therein greatly exceeds the limit of the solubility of the sodium sulfate in water (5). The effect of potassium sulfate is still more conspicuous in that respect on account of its low solubility compared with the sodium sulfate.

The chief impact of the examples mentioned on our conception of the chrome tanning process as it is carried out in concentrated solutions of ordinary chrome liquors of basic chromium sulfates is that the skin structure will remove from the solution and sorb less reactive noncationic chromium

complexes in addition to the normal, irreversible fixation of cationic chromium complexes with strong affinity for collagen. By washing and other secondary treatments that disturb the equilibrium of the system, protolysis of the non-cationic chromium compounds sets in, by which cationic chromium complexes are formed. Thereby, additional chromium complexes of strong tanning power are supplied (6). The final results will eventually be the effectuation of a straight cationic chrome tannage, i.e., very much the same type of leather as obtained by tanning with moderately concentrated solution of basic chromium sulfate. This brief outline of the behavior of concentrated solutions of basic chromium sulfates toward skin collagen is included in order to supply a background to the following discussion.

EXPERIMENTAL AND RESULTS

With due regard to the binding capacity of collagen for sulfuric acid and the degree of discharge of the carboxyl ions of the collagen at the pH range figured to be established in the solution of chrome alum by the protons resulting from the protolysis of the chromium sulfate, preliminary experiments indicated the optimal conditions, which are given in the following, for tanning of pelt with chrome alum *per se* without addition of water.

The guiding principle is to remove a sufficient quantity of the sulfuric acid resulting from the foregoing protolysis of the solution of the chromium sulfate held within the pelt, by the *collagen* to yield a 67% acid chromium sulfate. Concurrently, the incorporation with collagen of an amount of chromium of at least 3.5% Cr_2O_3, on the basis of collagen, must be upheld for securing the required degree of stability of the skin (tanning). The following procedure was found to give optimal conditions for such a tannage.

A thin calfskin split (pelt), which had been thoroughly delimed, subsequently equilibrated at pH 5.0 (boric acid solution) and washed carefully (ash content $<0.1\%$ of the dry weight) was squeezed out and then set out on a glass plate. Finally, it was lightly touched between filter paper. This procedure of removal of water was adjusted to yield a pelt with about 30% of dry substance (collagen). The pelt was cut up in strips (50 x 10 mm). To each series an amount of 10 g. of moist pelt, which contained 2.97 g. of collagen was used. The pieces were slicked out. Then 1 g. of chrome alum $Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$, in the form of a fine powder, was sprinkled evenly on both sides of the pelt. The skin specimens and any loose chrome alum powder were transferred into glass bottles and shaken horizontally at high speed (about 200 strokes per minute) for one hour up to 4 hours. All samples were left in the bottles for at least 2 hours before being analyzed. Some of the samples were kept in the bottles for longer periods, up to 48 hours. An even distribution of chromium in the pelt resulted in all instances. Strips were taken out, pressed, and their shrinkage temperature determined by the shocking method (4), i.e., by inserting the strips on a shrinkage meter in

water held at the temperature range of immediate shrinkage of the chromed pelt, which temperature range was ascertained by preliminary trials. Some specimens were squeezed out, washed, and shaken five consecutive times in 500 ml. of water, each treatment lasting 30 min. By this procedure a practically complete removal of uncombined chromium was obtained. The shrinkage temperature of the washed specimens was determined by the shocking method as well by the conventional method, applying a slow rate of heating of the sample, about a 3° C. rise of the temperature per minute. The two methods gave identical shrinkage temperatures, indicating completely stabilized chrome-collagen compounds. The results are presented in Table I.

TABLE I

SHRINKAGE TEMPERATURES OF CHROME ALUM–TANNED PELT

No.	Time of tannage, hr.	Ts of unwashed stock by the shocking method, °C.	Ts of washed stock, °C.
1	1	83	92
2	2	83	92
3	4	85	93
4	12	86	95
5	24	88	98–99
6	48	90	99–100

By applying the ordinary method of Ts determination, i.e., by slow heating, commencing in water of 30° C. and raising the temperature of the water at a rate of 3° C. per minute, specimen No. 2 showed a shrinkage temperature of 90° C. Hence, during the twenty minutes required for the attainment of the range of the shrinkage temperature, the redistribution of the chromium sulfate in the pelt and the removal of the unfixed chromium as well as protolysis products had imparted an additioned tanning effect, probably due to the fixation of the additional cationic chromium complexes formed by the concurrent protolysis of the tanning agent and to the removal of acid, making additional carboxyl ions of collagen available for the fixation of the cationic chromium complexes formed. By thorough washing, the final state of combination had evidently been obtained.

A typical record of the results from a chemical analysis of the chromed stock is given in Table II. The data pertain to tanned pelt in: (I) the original state, omitting any pressing and washing, (II) after rinsing in water for a few seconds and light pressing, and (III) after the complete washing procedure, as described, after 24 hours' tanning.

TABLE II

CHEMICAL COMPOSITION OF CHROME ALUM–TANNED PELT

No.	Type	Ash*	Cr_2O_3*	Combined Sulfate as SO_4	Collagen*	%Cr_2O_3 Fixed by Collagen	% Acidity of Chrome-Collagen Compound
I	Directly from tanning	8.3	4.2	8.1	81.6	5.1	102
II	Lightly rinsed and pressed	6.0	3.5	7.8	86.1	4.1	117
III	Thoroughly washed	3.5	3.3	4.0	92.8	3.6	64

*In percent on dry substance.

The sulfate of the washed specimen (III) was present in a quantity of 2% SO_4 in complex binding with chromium (*sulfato* groups), estimated by the pyridine method; the rest, or 2% SO_4, in the noncomplex form, probably mainly associated with the protein. The values are on the weight of collagen. The average acidity of the fixed sulfato-chromium complexes was 32%.

It should be noted that the composition of the chromed pelt in its original state conforms with the values deduced from the amounts of collagen and chrome alum employed. By a light rinsing and pressing of the tanned stock in order to remove the main part of the mechanically held chrome alum, the preferential removal of potassium ions is noteworthy, as shown by the difference in the figures of ash and Cr_2O_3, as well as by the figures (not included in the table for reasons of space) for neutral sulfate, K_2SO_4. This decrease in potassium ions is closely connected with the increased percentage of acidity of the corresponding chrome-collagen-compound, due to the formation of sulfato-chromiates. A value of 117% is recorded, whereas for the original stock the figure is 102%. The composition of the washed specimens corresponds to that of leather tanned by a conventional cationic chrome tannage. The excellent hydrothermal stability, evident by a shrinkage temperature of 98° C., is of interest in view of such a comparatively low chromium content as 3.6% Cr_2O_3, figured on the weight of collagen.

In order to ascertain whether an anomalous acidity of the original chrome alum–tanned pelt might be responsible for the low Ts recorded by the shocking method, the following experiment was devised. It was first established that the pelt fixed 0.78 meq. of sulfuric acid per g. of collagen on shaking one g. of collagen, in the form of pelt, in 25 ml. of 0.1*N* solution of sulfuric acid, containing 5 w/v % Na_2SO_4, for 10 minutes. Thus, about 80% of the binding capacity of collagen for sulfuric acid was satisfied during the brief period selected for interaction, in order to minimize secondary reactions of the sulfuric acid with the chromium complexes of the tanned stock which was to be tested by this method. By treating a sample of the washed chrome leather in a quantity corresponding to one g. of collagen with sulfuric acid

according to the procedure described for untanned pelt., the acid-binding capacity of the collagen in the tanned state should be expected to be nearly satisfied also. The Ts of the acid-treated leather was 94° C. Hence, it is evident that the low shrinkage temperature recorded for the original stock, omitting washing, is not likely due to any accumulation of sulfuric acid, or to the high acidity percentage of the chrome-collagen–compound formed by incorporating the chrome alum with the hide protein.

DISCUSSION

As to the complex composition of concentrated solutions of chrome alum in the freshly prepared state, the presence of noncationic chromium, including negatively charged chromium complexes, has been indicated by electrophoresis of short duration (7) and also by the ion-exchange technique, operating rapidly by the shaking method (8) as well as by the column technique (9) with the cation exchanger Dowex-50 as the sodium salt, and with the anion-exchanging resin Amberlite IRA-400 in the form of the chloride (10). Thus, for instance, by shaking one g. of dry Dowex-50 as Na-salt, hydrated in 5 ml. H_2O, with 200 mg. of the chrome alum powder for 10 minutes, 21% of the amount of chromium given was not taken up by the resin. In the corresponding series with the same amount of Cr_2O_3 in the form of hexaquo-chromium chloride, complete removal of chromium from the solution was obtained. In the anion exchange, 89% of the chromium given in the form of chrome alum was present in the filtrate. Thus the freshly dissolved chrome alum consisted of 79% of cationic complexes, 10% of nonionic chromium, and 11% of anionic chromium complexes. Since the formation of cationic chromium complexes occurs very rapidly, the figures given for the noncationic complexes only indicate the trend, on account of the long time required for the separation of the complexes.

The X-ray absorption spectra of various chromium compounds are of particular interest in this connection (11). The K-absorption edge of chrome alum crystals differs entirely from the absorption edge of the hexaquo-chromium compounds and the corresponding triethylene-diamine compounds. Actually the spectrum of chrome alum shows striking similarity to that of the oxalato-chromiates in which chromium is present in negatively charged complexes. Moreover, at the recent Faraday Society Discussion on the "Ions of Transition Elements", Sugano and Tanabe (12), who have investigated the line spectra of Cr^{3+} ions in crystals, stressed the difficulty of ascribing the lines of chrome alum to those of $Cr(H_2O)^{3+}$ compounds. Evidently, the crystal structure findings support the thesis of the sulfato-chromiate pattern of chrome alum.

In view of the previous presentation, the following possibilities of reactions between the chrome alum which has been merely dissolved in the skin struc-

ture are to be recognized: (*a*) The protolysis of the chrome alum and the removal of a part of its SO_4 ions by the electropositive groups of collagen. Concurrently the corresponding protons will be attracted to the carboxyl ions of the protein. (*b*) The basic chromium sulfate formed, containing complexes of the type $Cr_2(OH)_2SO_4^{2+}$, will be discharged by the carboxyl ions of the protein, becoming irreversibly attached to the collagen. (*c*) The sulfato-chromiate complexes, as the $Cr_2(SO_4)_4^{2-}$ anions are being attracted to and compensated by the electropositive protein groups. The potassium cations of the sulfato-chromiate will be electrostatically compensated by the carboxyl ions of collagen merely.

By the removal of the excess of the uncombined chrome alum by a light rinsing and pressing of the chromed pelt, the potassium ions appear to be preferentially removed, being displaced by protolysis. The hydroxyl ions formed will be taken care of by the uncombined chromium salt. On the other hand, by the prolonged washing of the chromed pelt, the anionic and nonionic chromium complexes are decomposed by protolysis and thus turned into electropositive chromium complexes which can combine with the collagen, the extent of their reaction being governed by the size of their charge and the number of free carboxyl ions available in the collagen at the pH value concerned. This is indicated to be in the vicinity of pH 2.5. The final result is a straight cationic chrome tannage in this instance.

The possible reaction types, which probably occur concurrently, may then be represented schematically by the following simplified equations. The skin protein is represented by the $(\overline{COO})_2 \cdot P \cdot (\overset{+}{N}H_3)_2$ structure.

I. $$(\overline{COO})_2 \cdot P \cdot (\overset{+}{N}H_3)_2 + 2\,\overset{+}{H} + SO_4^{2-} \longrightarrow (HCOO)_2 \cdot P \cdot (\overset{+}{N}H_3)_2 \cdot SO_4^{2-}$$

II. $$(\overline{COO})_2 \cdot P \cdot (\overset{+}{N}H_3)_2 + (Cr_2(OH)_2SO_4)^{2+} + SO_4^{2-} \longrightarrow \left(Cr_2(OH)_2 \begin{matrix} SO_4 \\ (COO)_2 \end{matrix}\right) \cdot P \cdot (\overset{+}{N}H_3)_2 \cdot SO_4^{2-}$$

III. $$(\overline{COO})_2 \cdot P \cdot (\overset{+}{N}H_3)_2 + 2\,K^+ + (Cr_2(SO_4)_4)^{2-} \longrightarrow K_2^+(\overline{COO})_2 \cdot P \cdot (\overset{+}{N}H_3)_2(Cr_2(SO_4)_4)^{2-}$$

By light rinsing, the following reaction is assumed to take place:

IV. $$\overset{+}{K}_2(\overline{COO})_2 \cdot P \cdot (\overset{+}{N}H_3)_2(Cr_2(SO_4)_4)^{2-} + 2H_2O \longrightarrow (HCOO)_2 \cdot P \cdot (NH_3^+)_2(Cr_2(SO_4)_4)^{2-} + 2\,K^+ + 2\,OH^-$$

The hydroxyl ion liberated should be taken care of by the excess of chromium sulfate present, forming basic chromium sulfate.

The question may be raised whether any reaction of protein-complex-compounds of this type is known, i.e., the removal of the metal cation compensating the anion attached to the electropositive protein groups. Actually, that is the case. On the fixation of the sodium or barium salts of the high-molecular α-ligninsulfonic acids by collagen from solutions of pH values in the range of 6 to 7, the original salt, which contains one atom of Ba per 2 atoms of S, is taken up by the collagen. On washing, the main part of the barium ions which are electrostatically compensated by the carboxyl ions of the protein are removed, whereas the polyacid anions associated with the electropositive protein groups are irreversibly fixed (13, 14). Thus, the final ligninsulfonate-collagen compound contains only 0.2–0.3 atoms of Ba per 2 atoms of S in the fixed ligninsulfonate. That is, 70–80% of the Ba ions are easily removed by protolysis, being displaced by the protons, which form the stable HCOO-group (13). In this particular example the polyacid anion is very firmly fixed by the collagen. Although the valency forces effecting the combination of the sulfato-chromiate ions with the positively charged groups of collagen are much weaker than those involved in the anchorage of the ligninsulfonate ions to the protein, the example given substantiates the occurence of reactions of the type postulated in the reaction scheme of type IV. The high affinity of the proton for the carboxyl ion, versus the mere electrostatic compensation of the cations of alkali metals such as K^+, must also be recognized.

A remarkable feature of this method is the introduction of a simple chromium salt evenly into and throughout the skin. The subsequent formation of the tanning agent takes place within the protein. The tanning effect is further augmented by the conventional washing of the leather.

ACKNOWLEDGMENT

The present problem, which discloses interesting theoretical issues as well as technical possibilities, was called to the author's attention by Mr. Georg Wolgien, AB. Glacéläderfabriken, Kävlinge, Sweden, in 1951. This investigation was then carried out, following up his suggestion, for which the author expresses his thanks. A grant from *Statens Tekniska Forskningsrad* is gratefully acknowledged.

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We need well-rounded men as the leaders of the next generation, skilled in science, law, medicine; skilled in organization and the complex relations between men in a modern society, with an understanding of history and an appreciation of art at its best. True, we need specialists as well, and many of these, if they are to extend the boundaries of knowledge, must devote themselves so assiduously to their specialities that they will have little time for great breadth of understanding. But even these must live in an intellectual atmosphere which is both broad and deep, where true accomplishment of seasoned minds is everywhere respected, and where youth will be caused to seek to emulate the full man. In the creation of this atmosphere we can all have a part. —Vannevar Bush.

The first leather tanning by the "oil tan" method of preparing buckskin and other leathers was originated by Talmadge Edward in Johnstown, N. Y., in 1810.

—*Famous First Facts*, Joseph Nathan Kane, The H. W. Wilson Company, New York, 1950.

Members of the community of science and scholarship necessarily think beyond national frontiers, and back across the sweep of man's experience. They know that nature does not give out her secrets with political discrimination. The brilliant innovator understands his debt to men of many countries and other centuries, and part of his satisfaction is in knowing that men unknown to him will build upon or supplant his work. Moderation and humility are in the environment, for the community's raison d'être is the discovery of truth and the exposure of error, including one's own. The assertion of personal or national interest is largely ineffective and ambition is subject to the disciplined discrimination with which the community bestows its respect.

—Rockefeller Foundation Annual Report, 1957.

LIFE LINES

Brief Biographies of Our Contributors

MRS. JEANNE G. FEE is engaged in research on the physical properties of hide and leather at the Eastern Regional Research Laboratory of the U. S. Department of Agriculture. A 1952 graduate of Davis and Elkins College, Elkins, West Virginia, she was on the staff of the National Bureau of Standards for two years before assuming her present position.

DR. K. H. GUSTAVSON is too well known to require an extended biographical note. He is universally recognized as one of the foremost leather chemists of our time. His chief interest is chrome tanning, but he has made numerous and important contributions to nearly every stage of leather manufacture. "Gus" spent some ten years in this country in the 1920's and early 1930's, during which period he was an active member of ALCA and a copious contributor to this *Journal*. He returned to Sweden in the mid-30's and is now Director of the Tanning Research Institute in Stockholm.

DR. LEE P. WITNAUER, a graduate of Canisius College and Temple University, joined the staff of the Eastern Regional Research Laboratory of the U. S. Department of Agriculture as a Junior Chemist in 1943. He is now Supervisor of the Physical Testing Unit of the Analytical, Physical Chemical and Physics Section. He is also an Assistant Adjunct Professor of Chemistry at Drexel Institute of Technology. Dr. Witnauer has recently been awarded the ALCA $1,000 prize for a paper which he will present at the meeting of the International Union of Leather Chemists' Societies in Munich in September. Title of his paper is "Dynamic Electrical Behavior of Untanned Hide Containing Sorbed Water".

Knowledge is power, and power which can not escape the calculus of political rivalry. But a misunderstanding of the nature of knowledge can lead to unwise and self-defeating restrictions upon intellectual life. Transitory advantage to a particular nation may, indeed, result from new discoveries but scientists around the globe promptly occupy the new terrain. Dr. Warren Weaver asks, "Will we recognize that, in the realm of pure science, you cannot keep a secret—that all you can hope to do is to keep ahead?" Perhaps one might add: and keep ahead in relatively short spurts.

—Rockefeller Foundation Annual Report, 1957.

Perhaps the first chemical society in the world was the Chemical Society of Philadelphia, founded in 1792 by James Woodhouse.

The first chemical element to be isolated in the United States was protactinium oxide, isolated in 1934 by Aristid von Grosse of the Kent Chemical Laboratory, Chicago.

ALCA NEWS

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SALES AND SERVICE REPRESENTATIVE WANTED by established leather finish manufacturer. Permanent position with excellent opportunity. Must have tannery background, be able to demonstrate in finish department, and be willing to travel principally east of Chicago. Sales or service experience preferred. Send full details and references. Information will be held in confidence. Our staff knows of this advertisement. Address replies to Box M-508, c/o Secretary, American Leather Chemists Association, University of Cincinnati, Cincinnati 21, Ohio.

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SECRETARY'S NOTICE

The following notes or changes in methods are for insertion in our Methods Booklet:

Method H-31 "Saponification Value"

Paragraph 4.3—modify to read

"approximately one hour for normal samples."

The following note is to be added:

"Some samples particularly difficult to saponify may require more than one hour. This can only be determined by trial. Clarity and homogeneity of the test solution are partial indicators of complete saponification, but they are not necessarily absolute criteria."

Method H-32 "Iodine Value—Wijs Method"
Paragraph 3.18—add following:

"All Wijs solutions are sensitive to temperature, moisture and light. Store them in a cool and dark place and never allow them to come to a temperature much above 30° C."

Method C-1 "Chromic Oxide"
Paragraph 4.1.1—modify to read

"The nitric acid may be omitted from the oxidizing mixture if organic matter is known to be low or absent."

Note: The Methods Booklets have been sent only to active members. Other members and subscribers may purchase these methods through the Secretary's office for $2.00.

REPORT

of the

SUBCOMMITTEE ON FATS AND OILS

The Subcommittee on Fats and Oils* proposes the following method of analysis for free and combined oil of chrome and chrome retan leathers. The committee also requests that any ALCA member who has worked on or worked out a combined oil determination for other types of leather submit such information to the subcommittee for consideration and possible inclusion in the Official Methods.

PROPOSED METHOD OF ANALYSIS FOR FREE AND COMBINED OIL OF CHROME AND CHROME RETAN LEATHERS

Apparatus shall be as given in 3.1, 3.2, 3.3, and 3.4 of ALCA Method B4.

FREE OIL

Procedure.—Weigh 5 g. of sample to nearest 0.01 g., and transfer to a cellulose extraction thimble. Cover leather with a pad of cotton, and then insert thimble into extraction tube. The extraction flask which has been dried by heating for 1 hr. at 99° ± 1° C., cooled 30 min. in a desiccator, and weighed, shall be connected to the extractor tube. Pour 250 ml. of chloroform into extractor tube so that solvent siphons into extraction flask. Connect tube and flask with condenser, and place assembly on hot plate already up to temperature. Keep temperature of hot plate at such a point that solvent siphons from tube every 10 ± 3 min. Run extraction until all fat has been recovered. This will require a minimum of 5 hr. extraction.

Disassemble apparatus, remove thimble from extraction tube, and distill off bulk of solvent, leaving about 30 ml. in flask. Remove remainder of chloroform by placing flask on steam bath. Heat until odor of solvent can no longer be detected. (Cooling of flask to room temperature often aids detection of traces of solvent.) Slight blowing with air may be used to remove the last portion of solvent.

Place flask on side in forced-draft oven at 99° ± 1° C. for 90 min., cool in a desiccator 30-60 min., and weigh.

Return flask to oven, heat 60 min., place in a desiccator for 30-60 min., and weigh. Continue heating for the number of times required to bring flask to constant weight.

*Chairman: Merrill R. Leach; *members*: C. A. Blair, G. A. Butz, B. A. Grota, Jr., V. Mattei, C. M. Morrison, Jr., C. E. Retzsch, and T. Weaver.

COMBINED OIL

Procedure.—Quantitatively transfer solvent-free extracted leather from thimble to a 500-ml. Erlenmeyer flask. Add 100 ml. of 5% NaOH. Digest on a hot plate with refluxing for 2 hr. using an air condenser and temperature of 300°-375° F. Cool slightly, add 50 ml. of 20% (by weight) H_2SO_4, and continue heating for an additional hour.

Cool to room temperature, and transfer to a 500-ml. separatory funnel. Shake vigorously with 150 ml. of ethyl ether. Rinse digestion flask free of oil with each portion of ether used for extraction. Draw off acid-water layer, and extract with 4 successive 75-ml. portions of ethyl ether. Any insoluble matter should be drawn into the water layer. Combine the 5 ether extractions, and wash with water until free of acidity.

Filter ether through semi-fine filter paper into evaporation flask. Wash filter thoroughly with ether to remove all traces of oil. Evaporate off ether, and weigh residual oil after drying 90 min. at 105° ± 1° C. in a forced-draft oven and cooling 30-60 min. in a desiccator. In drying down ether extract, do not blow with air, but add 10 ml. of isopropyl alcohol to remove last traces of water in the flask. Return flask to oven, heat 30 min., place in desiccator for 30-60 min., and weigh. Continue heating for the number of times required to bring flask to constant weight.

Dissolve residual oil from final weighing with fresh ethyl ether. If all residue dissolves, consider all of residue as combined oil. If ethyl ether solution is cloudy, filter solution through semi-fine filter paper into evaporation flask. Rinse out solution several times with ethyl ether, and wash filter paper until all traces of solution and oil have been removed. Evaporate ether, and weigh as combined oil after drying 60 min. at 105° ± 1° C. and cooling 30-60 min. in a desiccator. Repeat heating—using 30-min. periods—for the number of times required to bring flask to constant weight.

Any oil present in the leather as an ester will be converted to a fatty acid in this determination. A gram of oleic acid is equivalent to 1.045 g. of its glycerine triester.

ALCA-ASTM JOINT COMMITTEE ON LEATHER

Meeting March 19–20, 1959

Willard Hotel
Washington, D. C.

The subcommittee and section meetings began at 10:00 A.M. on March 19 and continued to noon, March 20, 1959.

The Joint Committee convened at 1:00 P.M., March 20. The first order of business was the presentation of reports of meetings of subcommittees and sections, copies of which are appended.

The Advisory Committee convened at 3:00 P.M., March 20. The first order of business was the consideration of a proposed change in the organization of the committee in which each section of Subcommittee III would become a subcommittee. The proposal will be considered further at a later date.

The annual report of the Joint Committee, to be prepared by Dr. Kanagy, is expected to include two new tentative methods for Thickness of Units and Bond Strength of Leather Belting.

A special report on "The Interlaboratory Evaluation of Testing Methods" presented by John Mandel, National Bureau of Standards, described and illustrated a new method for the analysis of interlaboratory tests. This proved to be a subject of considerable interest as indicated by the lengthy discussion and comments. An abstract of the report is attached.

The next meeting of the Joint Committee will be held in Philadelphia during November 1959.

C. W. MANN
Secretary

Subcommittee I. Nomenclature, Definitions and Applicability.—This committee did not hold a formal meeting, since no items were presented for action. However, its members did participate in the panel discussion on "Significance and Precision of Test Methods."

The subcommittee has cooperated with the several technical sections during the past months in the development of significance and precision statements. However, only two items have progressed to the point where methods can be written at this time. A method for the Bond Strength of Belting Leather developed by the National Industrial Leathers Association and the Mechanical Leathers Section was supplied with a significance section. Tentative approval has been given to precision and significance sections of the "Proposed Method of Determining the Thickness of Units." This method is to be rewritten to include revisions desired by Subcommittee I.

R. M. LOLLAR

Subcommittee II. Sampling and Conditioning for Physical Testing.—The committee did not hold a formal meeting, but the members discussed the work in progress on the sampling of small skins and on the preparation of a procedure for interlaboratory testing of leather.

C. W. MANN

Subcommittee III.—*Section 2. Physical Dimensions.*—The committee had one of its best meetings, with three members and four guests actively participating. The proposed draft of a Method for Measuring Thickness of Units was reviewed in the light of comments received from members when the method was circularized. To obtain a wider audience, members familiar with practices in the heavy leather trade were also circularized. Two persons responded with helpful comments which were incorporated along with other changes. The modified draft will be submitted to the Subcommittee on Nomenclature, Definitions and Applicability.

J. NAGHSKI

Section 3. Tensile Properties.—Two members of the committee and two visitors were present at the meeting. The following work was discussed, and work will continue on these methods:

1. Mullen Test and Ball Burst Method.—The only difference in machines is that Model A is motor-driven and the Jumbo Model is hand-operated. The members present agreed that the hand-operated machine should be adopted because of better control. An investigation will be made as to the use of a hydraulic motor drive because of the slower drive. The speed of the hand-operated machine will be studied, with the thought in mind that speed should slow down considerably as the pressure is applied to crack the grain. The use of a gauge to measure the distension of leather will be incorporated into the method. (Gauges can be added to the Mullen Tester very easily.)

The Ball Burst concordance tests are in process; this time the grain crack by the Ball Burst machine and grain crack by the Mullen Tester are being run on the same samples. When the tests are complete, evaluation of the two grain crack methods will be made. The committee feels that a ½"-diameter plunger should be investigated to get better correlation between the instruments, and this will be done. The Olson Burst Tester will be included in the investigation. Gauges for measuring distension of leather should be available for all machines.

2. Method E12 (Stitch Tear, Single Hole) will be investigated as to the distance of the hole from edge of sample. In Method E13 (Stitch Tear, Double Hole) the diameter of the wire for pull-through should be changed in method to the diameter of 0.038 ± 0.001, since most of the paper clip wires used will have this diameter.

3. All of the tear-type methods will be investigated as to usefulness. Some of the methods are similar and give the same end results, so a revision will be made with the possibility of dropping or tabling some of the methods.

4. Significance.—One committee member submitted significance sections for each method. These were discussed, and some definitions were revised. More significance sections will be submitted by the committee members before final writing into the methods.

Progress is being made on these methods, and perhaps we may have some ready for the Joint Committee by the next meeting.

Section 4. Measurement of Water Resistance.

1. Water Absorption, Static.—The Committee voted to change the method from a weight to a volume basis which should more accurately reflect the water absorption of sole leather of different densities. The modified method will be submitted to the section for acceptance.

2. Water Penetration, Dynamic (Upper Leathers).—Charles Dudley has volunteered to combine the ALCA and Federal Specification methods for the Maeser test, incorporating the electronic end-point determination. Both this method and the alternate Dow Corning method will be held up pending a statement on precision which may be developed by a review of the paper by Lollar and Maeser.

3. Water Penetration, Dynamic (Heavy Leather).—The Bureau of Standards has completed testing samples of various leathers submitted by Arthur Kay. The apparatus has been sent to him, and he will, in turn, send it on to Wagoner after he has completed his tests.

4. Garment Leather.—A method for a spray test has been written up and will be submitted for approval. Considerable laboratory work has been performed on an immersion test using whole skins. Six skins of each of three kinds have been tested in each of four laboratories. The method will be submitted to the section for approval.

5. Shoe Tester.—Thirty pairs of boots will be made up, using Sylflex leather and vulcanized bottoms, to investigate the correlation between the Dow Corning Shoe Tester and the wading test used by Charles W. Mann.

R. G. Ashcraft

Section 5. Surface Characteristics.—Two methods have been approved by the section in principle, and most of the disagreements on significance have been resolved. It is anticipated that these two methods will be ready for main committee action in the next two months. The methods are: Tentative Method for Flex Testing of Finish on Upholstery Leather and Cold Test of Finish on Upholstery Leather.

Tests are under way in the section to determine the best methods for flex testing of leathers other than upholstery. Tests have also been approved for studying the method of crock on all types of leather as well as the pendulum method for scuff testing. The large-scale lightfastness test is about one quarter completed; the completion date for this project is more than a year away.

The section had been asked by the main committee to study E44 (Staining) but decided to forego direct testing of this method pending a review of the general problem and presently available methods to test the same variable. The section also recommends that this method not be classed as staining but that the word staining be reserved for color or appearance changes of leather produced by other materials.

R. STUBBINGS

Section 6. Fire Resistance.—Inactive.

Section 7. Mechanical Leathers.—A quorum of seven members and guests discussed the initial draft of a procedure for determining the area shrinkage of leather. Several modifications were made and are being given further consideration. The procedure will be rewritten and then evaluated by Dr. A. Hirsch, Charles Dudley, and the chairman in an attempt to obtain data for determining precision.

The section gave final approval to a Proposed Test Method to Determine the Bond Strength of Leather Belting. The procedure was passed on to the chairman of the Joint Committee for further action.

A. N. COMPTON

Section 8. Deterioration Effects.—The following subjects were discussed:

1. Method of Test for Perspiration Resistance of Shoe Upper Leather.—A comparative test of KKL 311a—Method 3211 and the Roddy-Lollar method is now under way. The sampling plan was devised by Dr. W. Roddy (Tanners' Council Laboratory) to demonstrate adjacent and area-wise variation of both test methods. White leather only is being investigated in this initial study. A grain crack determination was added to Method 3211 to give comparative figures for each test.

2. Method of Test for Corrosive Chemicals.—It was determined that there are control test methods now in use for the action of corrosive chemicals on leather. Since several laboratories are engaged in this field, the committee agreed to delay the investigation.

3. Methods of Test for the Heat Stability of Leather.—The sampling plan, established by Charles W. Mann (Quartermaster Research and

Engineering Center), is as follows: (*a*) Five lots (six sides each) of different types of chrome side leather will be obtained and (*b*) three lots of water-resistant leather (Quilon, Scotchgard, and Sylflex) will be used. Equivalent lots of untreated leather will also be included.

Laboratory work will be done by (*a*) Charles Mann who will use the Climatic Chamber (exposure will be desert and tropical) and (*b*) James Cassel of the Bureau of Standards who will follow Federal Specification Method 3311. High humidity and moderate temperatures will also be investigated.

For the next meeting, Charles Mann will assemble information on the dry-heat stability of leather as it relates to the vulcanizing process.

4. Method of Test for Dry Cleaning Suede Leather.—W. Cooke (du-Pont) and Maynard Olson (Minnesota Mining and Manufacturing Company) will prepare a dry cleaning test method, based upon available information. This will be presented at the next meeting.

C. F. DUDLEY

Section 9. Disbanded.

Section 10. Miscellaneous Physical Properties.—Six members and a few guests were present. The following methods were considered:

Method E40 (Pipe)

Break.—M. Bailey is collecting twenty samples, varying over a wide range in coarseness of break, which he will send with his machine to eight different laboratories to be read. After the readings are complete, the data will be processed for significance, meaning, and accuracy of the instrument.

Piping of Upper Leather.—The members present still disagreed on what "piping" was. A clear definition should stress the differences that exist between "break" and "piping" characteristics.

M. Maeser had a number of upper leather strips taken from one skin which showed varying degrees of piping from practically a fine break to wrinkles 5/32" wide. No instrument would be required to read them. They were obtained by cementing pieces of upper leather to relatively stiff pieces of sole leather and stripping the pieces apart. The upper leather rolled back on itself with the grain inward, causing piping which was permanent. M. Bailey is going to try the method on a number of leathers.

Piping of Sole Leather.—The committee decided not to concern itself with the piping of sole leather. If interest in such a method should

develop next year, it will be taken up; otherwise it will probably be recommended to ALCA that the method be dropped.

Stiffness in Upper Leather.—J. Kanagy made a yoke to duplicate the test method described at the November, 1958, meeting, but the yoke was too heavy and is being made over.

Stiffness in Sole Leather.—ALCA Method E43 (Stiffness) will be written up in Joint Committee format by B. F. Lewis and submitted to the section membership before the next meeting.

Compressibility.—J. Bassett presented a report prepared by Mattei showing that the results of the compressibility test were not significantly affected by substantial changes in either the load or the time of dwell under load. A round-robin test will be planned by M. Battles and A. Kay to obtain the data necessary to establish the significance and accuracy of the method.

Indentation Hardness.—The section members feel that a great deal of information exists in the literature comparing the results of several indentation tests with the compressibility test, and that enough instruments and devices for making indentation tests are available. Anyone who wishes to make such tests may do so; the probable correlation between the indentation data which are obtained and the compression results can be found from published papers. The section decided that no work on indentation hardness was necessary or justified.

Method E41 (Grain Cracking).

The bar sizes recommended in Method E41 are to be changed to the nearest bright-drawn steel size to lower the cost of the apparatus, and the method will be written up by M. Maeser for presentation to the section members before the fall meeting.

Low-Temperature Properties.—The Surface Characteristics Subcommittee is developing a test for the resistance of leather finishes to cold cracking, so Section 10 is not interested in this problem.

This section was asked to consider a test for measuring some unspecified property or properties of leather at a temperature as low as that of liquid nitrogen or other gases. The committee feels that investigation of the properties of leather at low temperatures as compared to the properties of other materials under similar conditions would be an interesting research project, but until such time as there is a demand for a method of measuring some specific property under low temperature conditions, there is no justification for development of test methods. It was recommended that the problem be referred to the mechanical leather committee for its opinion as to the demand for such methods.

If that committee sees no need for any methods, the members of Section 10 suggest the matter be dropped.

M. MAESER

Subcommittee IV. Research.—A quorum of 11 members and 15 guests were present.

Some of the leather properties mentioned during the discussion of comfort at the meeting last fall were discussed at this current meeting.

C. W. Mann reported on the subject of moisture absorption from rate and equilibrium viewpoints, particularly in regard to the foot-sock-shoe system. In continuation he will review current tests and modifications thereof to see if a new test development should be recommended.

In connection with heat conductivity Dr. J. Kanagy reported that determinations of this property are in progress at the Bureau of Standards with a particular type of apparatus. It is planned that these data will be compared with those obtained with the Cenco Fitch apparatus. Anyone having Cenco Fitch data should send them to Dr. Kanagy.

The measurement of resilience was discussed by Dr. Lollar. It appears that measurement of this property would be of value in characterizing leather, possibly in connection with both tensile or ball burst tests during cyclic stress-strain studies. The compression type of test should be considered in this connection also. It was recommended that the Research Subcommittee suggest this as an area for study by research groups.

The discussion of electrical conductivity was postponed until the next meeting. There was a brief discussion of the superiority of resistance measurements over dielectric measurements for leather. The subject of heat of wetting was inadvertently omitted from the agenda; this topic will be taken up at the next meeting.

The difficulty of relating any of these properties to subjective appraisal, such as comfort, was reiterated. At present, correlation of these properties with subjective ratings is believed to be an area too complex and difficult for committee study. It was pointed out that the ASTM is planning a conference on subjective tests. Results of this meeting will be of particular interest to this committee. At present, it may be said that the Research Subcommittee does not plan to proceed further than to point out what additional properties of leather might be measured and to indicate how they might be measured. If any of these properties are of particular interest they may be suggested to the appropriate sections for further consideration.

M. Bailey listed a number of properties or terms used in rating leather and said he would keep the Research Subcommittee informed on the activity of his group in this area.

The applicability of nondestructive testing methods to leather was discussed briefly. It was recognized that this type of test would be of great value in quality control, but no specific method with possibilities of promise was suggested. This subject will receive continued attention.

M. M. BALDWIN

SPECIAL REPORT

THE INTERLABORATORY EVALUATION OF TESTING METHODS

JOHN MANDEL AND T. W. LASHOF

National Bureau of Standards

ABSTRACT

In this paper a new approach was presented for the analysis of interlaboratory studies of test methods. The various sources of variability in test methods were examined, and a new general scheme to account for them was proposed. The assumption was made that systematic differences exist between sets of measurements made by the same observer at different times or on different instruments or by different observers in the same or different laboratories, and that these systematic differences are linear functions of the magnitude of the measurements. Hence, the proposed scheme is called "the linear model". The linear model leads to a simple design for round-robin tests but requires a new method of statistical analysis geared to the practical objectives of a round robin. The design, analysis, and interpretation of a round robin in accordance with the linear model were presented, and the procedure was illustrated in terms of the data obtained in an interlaboratory study of the Bekk Smoothness Tester for paper. It is believed that this approach will overcome the "frustrations" that are often associated with the interpretation of round-robin test data.

The first chrome-tanned leather successfully marketed was produced in 1890 by Robert Herman Foerderer of Philadelphia.

The first patent leather was tanned in 1819 at Newark, N. J., by Seth Boyden.

ABSTRACTS

Spectrophotometric Studies in Leather Research. IX. Photometric Titration Method for Estimation of Salts of Weak Acids in Tan Liquors. A. Nagasiromani, D. Ramaswamy, and Y. Nayudamma. *Bull Central Leather Research Inst., Madras*, **5**, 1–11 (1958).—This is a modification of the method of Rehm and Higuchi (*Anal. Chem.*, **29**, 368 [1957]). When a weak base, e.g., the salt of a weak acid, is titrated with HCl in the presence of an indicator (metanil yellow) that is a much weaker base, the acid does not react appreciably with the indicator (I) to form IH^+ until most of the salt has been titrated. When IH^+/I is plotted against volume (X) of standard acid added, the X-axis intercept of the linear portion of the plot gives the volume of acid equivalent to the salts of weak acids. $(IH^+/I) = (A–A_b)/(A_a–A)$, where A_a is the absorbance of 530 mμ of the solution containing an excess acid, A_b the absorbance with no added acid, and A the absorbance in the presence of X ml. acid. Since the absorbance of tannin, as well as the indicator, changes with acidity, it is necessary to prepare 2 filtered 2%-tannin solutions, one with and one without metanil yellow, the latter serving as a blank. Both solutions are titrated with *N* HCl, and their absorbances are measured at 530 mμ after each addition of acid. Values for salts of weak acids were determined for white valem, dhawa, sumac, sulfited quebracho, wattle, myrobalans, chestnut, divi divi, avaram, goran, and arjuna. Results agree fairly well with those obtained by the potentiometric titration method (Burton and Bickley, *J. Soc. Leather Trades' Chemists*, **38**, 249 [1954]) and the nonaqueous titration method (Nayudamma and Ramaswamy, abstr. *JALCA*, **53**, 476 [1958]). The latter method apparently gives false results with sulfited quebracho. The method was validated by titrating known amounts of Na acetate, oxalate, citrate, tartrate, and gallate, alone, in mixtures, or added to tan liquors. H.B.M.

Studies on Shrinkage Phenomenon. III. Formaldehyde Combination Tannages. Y. Nayudamma and K. S. Jayaraman. *Bull. Central Leather Research Inst., Madras*, **5**, 91–97 (1958).—In previous work (abstr. *JALCA*, **52**, 100 [1957] it was shown that retannage with HCHO generally raises the T_s of leathers variously pretanned, which was attributed to additional cross linking by fixed HCHO. No determinations of fixed HCHO were made in the previous tests. In the current series, acetone-dehydrated and rehydrated pelt pieces were pretanned as follows: (1) with a syntan (Basyntan) at pH 2, (2) Calgon at pH 2.5, (3) basic Cr sulfate at pH 3.5, (4) Al sulfate at pH 4, (5) fish oil, (6) Immergan, (7) wattle at pH 4, and (8) myrobalans at pH 3.5. Specimens from pretannages 1–4, 7, and 8 were retanned with HCHO at the pH of the pretannage, and specimens from pretannages 1–6 were retanned with HCHO at pH 7. Pelt pieces were also tanned directly with HCHO at each of the pH values used for the HCHO retannage. T_s was determined before and after HCHO retannage. Combined HCHO was determined by the Highberger-Retzsch method in the leathers from pretannages 1–6, and by measuring the degree of exhaustion of the HCHO retan bath in the case of the leathers pretanned with wattle or myrobalans. For the 4 mineral pretannages, HCHO fixed at the lower pH values was the same or less than the amounts fixed at the same pH values without retannage. Calgon-pretanned skins fixed no HCHO, and this was the only leather for which T_s was not raised appreciably by HCHO

retannage. The small amounts of HCHO fixed at low pH values by leathers pretanned with syntan, Cr, and Al raised T_s by 8°–10°C. The leather pretanned with syntan fixed little more HCHO at pH 7 than at pH 2, which is explained by blockage of side chain NH_2 groups by the syntan. For all the other pretannages, retanned at pH 7, or pH 3.5–4 in the case of vegetable pretannages, much more HCHO was fixed than in the case of the non-pretanned controls. In the case of the Calgon, Cr, and Al pretannages, this is thought to be due to a "salt effect"; in the case of fish oil pretannage, to activation of arginine groups; in the case of Immergan pretannage, to activation of arginine or fixation at the sulfonamide linkage; and in the case of vegetable tannage, to formation of cross links between fixed tannin molecules. H.B.M.

Correlate Corrosion Testing Methods. R. V. Jelinek. *Chem. Eng.*, **66,** No. 2, 105–10 (1959).—Various types of corrosion tests are discussed rather than described, and their advantages and limitations are pointed out. 42 references. H.B.M.

Qualitative Aldehyde Reactions. Identification of Amino Acids. R. W. Storherr. *Anal. Chem.*, **31,** 268–70 (1959).—All amino acids react with 2-furaldehyde in glacial acetic acid solution to give absorption maxima at about 360–80 mμ, but the diamino acids lysine, hydroxylysine, and ornithine also give absorption maxima at 525–30 mμ. s-Trioxane reacts with hydroxyproline in glacial acetic acids to give a yellow color with absorption maximum at 492–94 mμ. The reaction is said to be specific for hydroxyproline, but a preponderance of other amino acids interferes with the reaction. The reaction is not quantitative, but it is a useful qualitative test, especially for distinguishing hydroxyproline from proline. H.B.M

Determination of Sulfides, Sulfites, and Thiosulfates in the Presence of One Another. A. P. Kreshkov and L. P. Senetskaya. *Nauch Doklady Vysshei Shkoly, Khim. v Khim. Tekhnol.*, **1958,** No. 1, 68–72; *Chem. Abstr.*, **53,** 981*f*.

The Swelling of Collagen and Its Prevention by Adenosinetriphosphate (ATP). J. Balo and I. Banga. *Magyar Tudomanyos Akad. Biol. Orvosi Tudomanyok Osztalyanak Kozlemenyei*, **9,** 75–86 (1958); *Chem. Abstr.*, **53,** 1428*h*.

Enzymes in the Skin: Their Use as a Research Tool. R. D. Griesemer. *J. Soc. Cosmetic Chemists*, **9,** 148–58 (1958); *Chem. Abstr.*, **53,** 1442*a*.

Synthetic Tannin No. 4. S. A. Kuraitis and S. K. Golubeva. *Legkaya Prom.*, **18,** No. 9, 23–26 (1958); *Chem. Abstr.* **53,** 1797*e*.

The Impregnation of Tannin Fixatives in the Production of Heavy Leathers. A. I. Metelkin. *Legkaya Prom.*, **18,** No. 9, 17–18 (1958); *Chem. Abstr.*, **53,** 1797*f*.

The Determination of Acrylic Resins in Leather. V. L. Voitsekhovskii and I. M. Fedorova. *Legkaya Prom.*, **18**, No. 9, 30–31 (1958); *Chem. Abstr.*, **53**, 1797g.

Black Wattle Catechin. D. G. Roux and A. E. Maihs. *Nature*, **182**, 1798 (1958).—The first isolation of a catechin (flavan-3-ol) of the resorcinol series from natural sources is recorded by the isolation of (–) – robinetinidol from black wattle bark (*Acacia mollissima*). R.M.L.

The Polypeptide Chain Configurations of Native and Denatured Collagen Fibers. E. M. Bradbury, R. E. Burge, J. T. Randall, and G. R. Wilkinson. *Configurations and Interactions of Macromolecules and Liquid Crystals. Discussions of the Faraday Society.* **No. 25**, 173–85 (1958).—A diffraction pattern calculated for structural model II of collagen is compared with the experimentally determined high-angle X-ray diffraction patterns for wet collagen. The diffraction pattern from collagen II was calculated assuming water molecules in every possible systematic position along the collagen main chain (approx. 25 g. water per 100 g. collagen). The calculations refer only to the diffraction pattern from the ordered regions along the collagen structure, i.e., region of short side chains, since the molecular configuration in regions of longer side chains is not necessarily that depicted in model I or II. Qualitative agreement between the calculated and experimental patterns is sufficient to indicate that major features of model II are correct. Some preliminary work on the infrared spectra of collagen denatured by a number of neutral salts is reported together with information about the configuration of the minor helices in specimens of thermally denatured collagen. A discussion is given of the existing relationship which exists between native collagen and thermally and salt-denatured collagen on the one hand and native collagen and hot-and-cold-cast gelatin on the other. This analysis is based mainly on the characteristic infrared absorption spectra of the materials, the dichroic ratios observed, and also the relative rates at which films a few microns thick of the different specimens are deuterated in an atmosphere of D_2O of relative humidity 100%. J.M.C.

Two Tripeptides from an Enzymatic Digest of Collagen. R. E. Schrohenloher, J. D. Ogle, and M. A. Logan. *J. Biol. Chem.*, **234**, 58–61 (1959).—A description is given of the isolation and identification of the tripeptides glycylprolylalanine and glycylprolylhydroxyproline, obtained on digestion of Achilles tendon collagen with *Clostridium histolyticum*. Collagen digests were prepared by incubation at 37°C. with five times the quantity of enzyme necessary to give complete solution of collagen. Ion-exchange and paper-chromatographic procedures were applied to isolate the peptides. The DNP end group tagging procedure was employed to determine the N-terminal residues and the phenylthiohydantoin procedure for the sequence of the tripeptides. Together, the tripeptides account for 10% of the nitrogen, 23% of the alanine, 14% of the glycine, 23% of the hydroxyproline, and 40% of the proline content of collagen. J.M.C.

The Relation of Ascorbic Acid to the Conversion of Proline to Hydroxyproline in the Synthesis of Collagen in the Carrageenan Granuloma. W. van B. Robertson, J. Hiwett, and C. Herman. *J. Biol. Chem.*,

234, 105–8 (1959).—Data are presented to show that conversion of proline to hydroxyproline is impaired in ascorbic acid–deficient guinea pigs. The results, however, are not readily reconciled with previously suggested mechanisms for the synthesis of hydroxyproline in the collagen molecule. After inducing carrageenan granulomas in guinea pigs, uniformly labeled proline-C^{14} was administered for 3 days, and proline and hydroxyproline were isolated from collagen and non-collagenous fractions of the granuloma and from serum proteins. In the ascorbic acid–deficient animals the concentration and specific activity of hydroxyproline in collagen were, respectively, 20% and 60% of the normal in contrast to values of 90% and 180% in animals recovering from the deficiency. The data do not support the hypothesis that a proline-rich, hydroxyproline-deficient precursor of collagen accumulates in vitamin-deficient granuloma. Since in several extracts the specific activity of hydroxyproline exceeded that of proline, the possibility exists of a pool of "active" hydroxyproline derived from, but distinct from, the proline pool. J.M.C.

The Effect of Some Manufacturing Factors in Leather Production on the Formation of Air Holes. N. A. Oreshkov. *Uchenyi Zapiski Beloruss. Inst. Narod. Khoz.*, **1955,** No. 1, 119–25; *Referat. Zhur., Khim.*, **1956,** Abstr. No. 49391; *Chem. Abstr.*, **53,** 3749*f*.

Synthetic Tanning Agents from Native (Bulgarian) Raw Materials. Y. Basan. *Khim. i. Ind.* (Sofia), **29,** No. 6, 17–20 (1957); *Chem. Abstr.*, **53,** 3749*d*.

The Determination of the Loss of Collagen in Leather Production. N. N. Stephanovich. *Legkaya Prom.*, **18,** No. 10, 37–9 (1958); *Chem. Abstr.*, **53,** 3749*i*.

The Tanning of Hides with Chrome Liquors Masked with Sodium Sulfite. S. G. Ponomarev and N. N. Oleinik. *Legkaya Prom.*, **18,** No. 10, 39–40 (1958); *Chem. Abstr.*, **53,** 3750*a*.

The Purification of Waste Waters from Tanneries. V. F. Shankin. *Legkaya Prom.*, **18,** No. 10, 44–5 (1958); *Chem. Abstr.*, **53,** 3750*e*.

Investigation of Green Modifications of Chromium Chloride Complexes by Means of Ion Exchange. N. S. Fokina. *Izvest. Vysshikh. Ucheb. Zavedenii, Tekhnol. Prom.*, **1958,** No. 2, 47–55; *Chem. Abstr.*, **53,** 2917*a*.

Aspects of the Electron Microscopy of Collagen Reconstituted from Solution. R. E. Burge, C. D. Curling, F. C. Kelly, and J. T. Randall. *Proc. Intern. Conf. Electron Microscopy, 3rd, London,* **1954,** 587–93 (1956); *Chem. Abstr.*, **53,** 3318*e*.

Bleaching of Marmot Fur. K. A. Barma. *Nauch.-Issledovatel. Trudy Nauch.-Issledovatel. Inst. Mekhovoi Prom.*, **6,** 161–73 (1955); *Referat. Zhur., Khim.*, **1956,** Abstr. No. 56792; *Chem. Abstr.*, **53,** 3702*h*. **Changes of Physical-Mechanical Properties of the Hair Mantle of Rabbit Skins as a Result of Tanning and Dyeing Processes.** G. P. Kadzharduzova. *Ibid.*, 129–37; Abstr. No. 56794; *Chem. Abstr.*, **53,** 3705*f*.

Stability of Lanthionine Formed during Attack of Alkali on Wool. M. van Overbeke, G. Decroix, and G. Mazingue. *Bull. Inst. Text. France*, No. **76**, 37–48 (1958); *Chem. Abstr.*, **53**, 3703*h*.

A Simple Qualitative Test for Syntans. A. N. Rosiera. *Bol. INT* (Inst. nacl. tecnol. Rio de Janiero), **6**, No. 14, 10–16 (1955); *Chem. Abstr.*, **53**, 3749*a*.

Improving the Quality of Willow Extract. M. N. Krasukhin, L. P. Pavlov, V. N. Rubakhin, and V. N. Torsuev. *Legkaya Prom.*, **18**, No. 10, 27–30 (1958); *Chem. Abstr.*, **53**, 3749*b*.

Fractionation of Tannin Substances with Adsorbents. V. M. Glezin. *Zhur. Priklad. Khim.*, **31**, 1554–60 (1958); *Chem. Abstr.*, **53**, 3749*c*.

Chemical Changes of Hide Substance under Liming and Bating Conditions. H. Hörmann and B. Schubert. *Das Leder*, **9**, 265–74 (1958).—The tanner, in order to avoid loss of hide substance, should know the extent of the action of lime and bates on collagen and other hide components. For a study of this problem purified collagen was used that had been prepared from the middle split of a beef hide and treated with trypsin and lime to remove noncollagenous material and damaged collagen residues. The lime and bate solutions in which the purified collagen had been treated were analysed for nitrogen, ammonia, and hydroxyproline. Very little nitrogenous matter was found in a saturated lime solution in which collagen had been treated at 20°–22°C. for up to 8 days. After 8 days the ammonia in the lime solution accounted for 75% of the amide groups originally present in the collagen. Appreciable amounts of hydroxyproline were found in solution only after 4 days, showing that lime does little damage to the peptide chain in less than 4 days. The hydroxyproline content of the 8-day lime liquor was 15% of the non-ammoniacal nitrogen. This is much above the 6.92% present in collagen and shows that lime had attacked a hydroxyproline-rich section of the collagen. This is surprising, because according to present theories the proline and hydroxyproline are in the more highly ordered, and therefore more resistant, parts of the fiber rather than in less crystalline and less resistant parts. Trypsin at pH 7.42 had no effect on unlimed collagen; but if the collagen had been limed for 1 or for 4 days, then after 8 hours' digestion with trypsin about 3% of the nitrogen in the collagen was found in solution. The decreased resistance to trypsin after a short liming was the result of swelling; but the trypsin solution decreased swelling so that its action gradually stopped. After collagen had been limed for 8 days, trypsin dissolved 5.2% of it in 2 hr., and tryptic action was increasing rather than decreasing after 24 hr. The high hydroxyproline content of the trypsin solution showed that collagen had been attacked during the 8-day liming period. Titrations with alcoholic potassium hydroxide were also made in order to study the effect of phosphate buffer and trypsin on collagen. This titration measures the increase in carboxyl groups formed during enzymatic splitting of peptide compounds. Some lime was retained by collagen after thorough washing with water. Part of this lime was removed by the buffer, but complete removal was obtained only after treatment with trypsin. The alkali requirement by titration of collagen

limed for 4 or 8 days was much greater than that of collagen limed for 1 day, although dissolved nitrogen from the 4-day-limed collagen was not much greater than that from 1-day-limed collagen. Possibly there is enzymatic splitting of compounds in the interior of the fibers, but the products do not go into solution because they are held in the peptide chains and by hydrogen bonds (topochemical hydrolysis). The behavior of raw hide to lime and trypsin was the same as for purified collagen except for the large amount of noncollagenous nitrogen removed in the initial stages of treatment. I.D.C.

Comments on the Investigations of G. H. Green on Bating. O. Grimm. *Das Leder*, **9**, 278–80 (1958); see *JALCA*, **52**, 164 (1957), **53**, 125, 224 (1958).—Green uses gelatin as substrate, but it is colloidal, and its viscosity, which he uses to measure enzyme activity, is influenced by numerous factors such as electrolyte content of the bate. Casein is quite uniform and preferable. Green's theory of the mechanism of bating states that lime changes collagen to progelatin, then heat at 40°–50°C. changes this to gelatin which is attacked by trypsin. This theory is not in accord with practice because much bating is done at 28°–30°C. It does not seem possible to have a general theory applicable to all kinds of skins and leathers. Not only do optimum conditions vary for the different kinds of skins required for the various types of leather, but the bating action within the skins themselves varies. The only common factor is the action on collagen. Because the action on albumins, globulins, mucoids, tropo- and procollagen, etc. differs so much, it is not possible to find a substrate for analytical use that has an action approaching that of the bate; therefore, it is best to use a substrate that has uniform, constant quality—preferably casein. Bating can not remove lime blast. Reuse of bate is not good practice because control of the process is then lost. An old bate should be reused only as a preliminary rinse. **The Mutual Action of Proteolytic Bate Enzymes in the Neutralization and Deswelling of Lime-swollen Hides. Comments on the Work of G. H. Green : The Mechanism of Bating.** A. Küntzel. *Ibid.*, 281–83 (1958); see preceding abstract.—To completely remove swelling from a limed hide, neutralization alone is not sufficient because of structural hysteresis. The network tension must be strengthened, and this is possible to some degree by the mechanical action in the float. The resistance of the swollen fibers must also be decreased, and this is accomplished by warming and by enzyme action. (Warming is primarily to remove swelling hysteresis, not to increase enzyme activity). Green's observation that mechanical action can produce a bating effect supports this idea. Lack of bating is evident in permanent drawn grain and a grain that is not as smooth and fine as that of a bated one, but not necessarily in hardness of the leather. Bate seems to act principally on the grain layer. A theory of bating involves a substrate, and possible substitutes in the hide are grain collagen, elastin, and hair musculature. These 3 can not be separated for individual study. Bating action appears to be a topochemical decomposition of collagen fibers, that is, a change in which no soluble products are formed. This does not agree with the theory of Green which postulates that bating removes a coating of progelatin from the hide fibers and so prevents adhesion of the fibers to each other after drying. Green, however, found no soluble collagenous protein in the bate liquors. Adhesion of fibers or lack of it is determined by the tannage, not by the bate. The prevalent view that the function

of a bate is to remove interfibrillary substance is not consistent with the fact that skins which have been soaked and unhaired with enzymes still require liming. The swelling that occurs in the lime must then be removed, and this is accomplished best by bating. I.D.C.

Oil in Preparation of Leather. A. N. Saha. *J. Indian Leather Technol. Assoc.*, **6,** 205–9 (1958).—A lecture on oiling and oil tannage. H.B.M.

Babul Bark and Possibilities of Its Extract Manufacture. R. R. Sondhi and O. P. Gulati. *J. Indian Leather Technol. Assoc.*, **6,** 210–14 (1958).—Manufacture of babul extract would reduce the huge tannin losses currently resulting from inefficient leaching of the bark. Satisfactory tannage with babul requires careful control of acid and salt concentrations, and the extract might be modified to make it more suitable. H.B.M.

Some Factors Affecting the Tensile Strength of Chrome-tanned Picking Band Leather. J. K. De and A. Chakravarty. *J. Indian Leather Technol. Assoc.*, **6,** 214–17 (1958).—The lower tensile strength of leather, compared to hide, is attributed to its lower water content. The rough inverse relationship between Cr content and strength is laid to increasing dehydration with increasing Cr. H.B.M.

The Economics of the Raw Materials Used, and Improved Techniques for, the Manufacture of Brown Picking Bands. A. S. Naik. *J. Indian Leather Technol. Assoc.*, **6,** 218–28 (1958).—This is a combination sulfur-oil-vegetable-tanned leather. The only suitable Indian raw material is the heaviest 25% of the buffalo hides. A short liming is preferred, followed by complete deliming, a heavy pickle, and depickling with $Na_2S_2O_3$ to deposit sulfur. Then the hides are stuffed twice with fish oil or a mixture of fish oil and tallow, followed by hot drying for 20–30 days. Vegetable tannage is done with quebracho (stated to be essential) and gambier or myrobalans, followed by yet a third stuffing. H.B.M.

Microdetermination of Ammonium and Protein Nitrogen. G. Fels and R. Veatch. *Anal. Chem.*, **31,** 451–52 (1959).—The protein is converted to ammonia by digestion with H_2SO_4 plus H_2O_2. The digest is neutralized to methyl red with NaOH and made to volume. Aliquots are treated with a reagent consisting of equal volumes of a 0.1*M* citrate buffer and 4% ninhydrin solution in methyl Cellusolve, heated to boiling for 20 min., cooled to 15°–20°C., and diluted with 1-propanol - water (1 : 1). The absorbance is read at 570 mμ. and NH_3 content is obtained from a standard curve made by measuring absorbances of solutions containing known amounts of $(NH_4)_2SO_4$. The method is less precise, but more sensitive and less laborious, than the Kjeldahl method and is more accurate and reproducible than the Nessler method. H.B.M.

Soluble Collagens. A. Delaunay and S. Bazin. *Rev. Rhum.*, **25,** 461–86 (1958); *Chem. Abstr.*, **53,** 2299*g*.

The Nature of Bonds Cleaved by Collagenase. O. V. Kazakova, V. N. Orekhovich, and V. O. Shpikiter. *Doklady Akad. Nauk S.S.S.R.*, **122,** 657–60 (1958); *Chem. Abstr.*, **53,** 2304*f*.

Water in Collagen. N. G. Esipova, N. S. Andreeva, and T. V. Gatovskaya. *Biofizika*, **3**, 529–40 (1958); *Chem. Abstr.*, **53**, 2324*e*.

The Structural Periodicity of Microscopic Collagen Fibers. A. J. Cruise. *Proc. Conf. Gelatine and Glue Research, Cambridge, Engl.*, **1957**, 45–49 (pub. 1958); *Chem. Abstr.*, **53**, 2325*b*.

The Position of Aldehydes in Collagen Molecules. J. M. Landucci, J. Pouradier, and M. Durante. *Proc. Conf. Gelatine and Glue Research, Cambridge, Engl.*, **1957**, 62–67 (pub. 1958); *Chem. Abstr.*, **53**, 2325*c*.

Preparation and Absorption of Basic Chromium-Aluminum Salts in the Combined Tanning of Sole Leather. D. Todor. *Ind. Usoara* (Bucharest), **5**, 330–34 (1958); *Chem. Abstr.*, **53**, 2664*d*.

Colorimetric Determination of the End Point in Titration of Tannins by the Lowenthal Method. V. Zitko. *Chem. Zvesti*, **12**, 533–42 (1958) (German summary); *Chem. Abstr.*, **53**, 2663*i*.

Warble Fly Control. Mary Dempsey. *J. Soc. Leather Trades' Chemists*, **43**, 26–30 (1959).—The important problem of hide damage by the warble fly is reviewed, and a brief account is given of the recently introduced systemic insecticides which show considerable promise. J.M.C.

Formation of Collagen Hydroxyproline *in Vitro*. N. M. Green and D. A. Lowther, *Biochem J.*, **71**, 55–66 (1959).—To study hydroxylation of proline in relation to collagen formation and to analyze the process in terms of current theories of protein synthesis, observations were made on granuloma induced in guinea pigs by subcutaneous injections of carrageenin. On incubation of the granuloma in the presence of L-(^{14}C) proline, both proline and hydroxyproline from the soluble and insoluble collagen fractions were labeled. After 4 hr. the total counts of proline and hydroxyproline from neutral-salt–soluble collagen were 20 times those in acid-soluble or insoluble collagen fractions, confirming that neutral-salt–soluble collagen represents an early stage in collagen-fiber formation. Addition of unlabeled hydroxyproline to the incubation medium in the presence of L-(^{14}C) proline had no effect on the ratio of the specific activities of collagen hydroxyproline and proline. Incubation of the tissue with L-(^{14}C) hydroxyproline did not result in a significant incorporation of radioactivity into collagen. Radioactive hydroxyproline was isolated from the tissue slices and medium after incubation with L-(^{14}C) proline but its specific activity was only half that of the neutral-salt–soluble collagen hydroxyproline, and the total counts present were not increased when unlabeled hydroxyproline was present as a trapping agent. From these observations it is concluded that free hydroxyproline is not an intermediate in the formation of hydroxyproline of collagen. J.M.C.

Criteria of Tannage. I. Experimental Studies on Shrinkage Temperature and Hydrothermal Stability. J. P. Danby and J. F. Shillito. *J. Soc. Leather Trades' Chemists*, **43**, 3–17 (1959).—After a brief review of the more important shrinkage temperature investigations and of methods of determining shrinkage temperature, current results based on a modified Chater

apparatus (similar in principle to the well-known Theis shrinkage meter) are discussed. The modified apparatus is particularly useful in testing very thin leather layers. The use of extension vs. temperature curves is discussed, and modifications due to rate of heating and to interruption in heating are given. The method for determining the shrinkage temperature of acid- or alkali-soaked leathers in toluene is discussed. In utilizing shrinkage temperature as a criterion of tannage one must be aware of at least four sources of error in the measurement: (1) a too slow rate of heating gives a low S.T.; (2) an inadequate soaking time, too high an S.T.; (3) a faulty selection of test sample, too high an S.T.; and (4) excessive tension applied, too high an S.T.

J.M.C.

A Study of the Affinity of Black Wattle Extract Constituents. V. An Investigation of the Fixation of Mimosa Tannins by Swollen Chemically Modified Collagen. R. L. Sykes. *J. Soc. Leather Trades' Chemists*, **43**, 17–26 (1959).—Previous papers (*JALCA*, **50**, 480, 617 [1955]; **52**, 295 [1957]) indicated that condensed tannin combination with hide is affected more seriously by chemical modification of tannin than by modification of the collagen. Changes in tannin fixation due to chemical modification of collagen were attributed to differences in swelling characteristics of the collagen. The present study provides quantitative data on these aspects of tanning. Employing miniature tannages of chemically modified pelt pieces, fixation of tannins was determined for various known degrees of swelling over the pH range 1.5–6.5 in the presence or absence of added salt. Deaminated, acetylated, esterified, and formaldehyde-treated hide sections (2 x 2 cm) were used. A plot of degree of tannage vs. degree of swelling prior to tannage compiled from data for untreated and modified hide sections indicates a general trend of increased tannin fixation with increased swelling capacity of the collagen. Application of statistics proved this trend to be significant. However, there was no simple or direct relationship between pH and tannin fixation. A plot of mean values for rise in shrinkage temperature vs. percent of fixed tannin gives a curvilinear approximation. Indication is that the amount of wattle tannin fixed, rather than site of fixation, determines hydrothermal stability of leather.

J.M.C.

Reaction of Sodium Borohydride with Wool. J. M. Gillespie. *Nature*, **183**, 322–23 (1959).—Sodium borohydride in alkaline solution rapidly dissolves wool under relatively mild conditions (92% wool dissolved after 1 hr. at 20°C. in 1*M* sodium borohydride with an initial pH of 11). The soluble material contains at least 3 proteins (separated by fractionation procedures and ultracentrifugation).

C.L.D.

Separation and Analysis of Scale-rich Material from Wool. J. H. Bradbury. *Nature*, **183**, 305–6 (1959).

Evaluation of the Effectiveness of Antibacterial Finishes for Cloth. P. A. Majors. *Am. Dyestuff Reptr.*, **48**, 91–3 (1959).—The antibacterial activity imparted to cotton cloth by treatment with various chemicals is determined by a method which closely parallels actual use conditions. It is based on the determination of titratable acid or alkali produced by the growth of the test organism in a buffered medium held in the interstices of the test fabric.

C.L.D.

The Determination of Damage to Wool Fibres. J. C. Brown. *J. Soc. Dyers Colourists*, **75,** 11–21 (1959).—A review is given of tests for damage to the wool fiber, including tests for modification of outer surface structure, for disulfide bond rupture, and for main chain degradation, as well as a new test for alkaline damage. C.L.D.

The Effect of Strain on the Electrical Resistance of Keratin. J. E. Algie. *Textile Research J.*, **29,** 1–6 (1959).—The effect of strain on the electrical resistance of keratin fibers was examined at 90% relative humidity and 20°C. The initial instantaneous increase in resistance (much greater than that due to dimensional change) was followed by a decrease and then a rise in resistance. These changes could be correlated with the moisture content of the fiber. C.L.D.

Possible Role of Water in Collagen Structure. R. D. B. Fraser and T. P. Macrae. *Nature*, **183,** 179–80 (1959).—From an investigation of the infrared spectra of two preparations of kangaroo tail collagen, one in equilibrium with the laboratory atmosphere and the other dried *in vacuo* at 100°C., it is concluded that the water molecules are probably linked through hydrogen bonds to some of the C=O linkages which are normal to the chain axis and project outward from the triple-chain molecule (and therefore are not available for intramolecular hydrogen bonding). C.L.D.

Collagen in the Perilemma of Insect Nerve. D. S. Smith and V. B. Wigglesworth. *Nature*, **183,** 127–28 (1959). C.L.D.

Colour Index. Additions and Amendments. *Am. Dyestuff Reptr.*, **48,** 56–62 (1959). C.L.D.

Nonionic Detergents in Raw Wool Scouring, Including Studies of Waste Clarification. W. Fong. *Am. Dyestuff Reptr.*, **48,** 45–50 (1959). C.L.D.

Protect Wool in Process. H. Laudani, G. O. Langlais, and F. E. White. *Am. Dyestuff Reptr.*, **48,** 42–3 (1959).—A low-cost method for protecting wool from insects by treatment with a mixture of 25% DDT, 10% Triton X-100, and 65% Solvesso 100 is discussed. C.L.D.

Buffing to Improve Leather—Means to a Better Product. D. Olton. *Leather & Shoes*, **135,** No. 4, 9 (1958).—The author describes the abrasives used in industry and the types of abrasive used in various buffing operations on side leather, nonslip linings, suede shoe uppers, sole leather, work shoe upper, calfskin, calfskin suede, goat and kid suede, garment sheepskin suede, and sheepskin suede shoe leathers. J.J.

Drying and Conditioning Methods in Today's Tanneries. M. Herman. *Leather & Shoes*, **135,** No. 5, 18 (1958).—This is a thorough analysis of the relative advantages and techniques involved in toggle, paste-drying, and electronic drying of skins. J.J.

Insecticide Stains on Leather. R. Hauck, R. Petruscke, and R. M. Lollar. *Leather & Shoes*, **137**, No. 2, 14 (1959).—An investigation of seven insecticides to determine staining on leather. While some staining was noted after liming and bating, no visible staining could be related to the insecticides after the leather was fatliquored and dried. J.J.

Recent Developments in the Field of Coating Colors. I. E. Eitel. *Leather Trades Rev.*, **129**, 418 (1958).—The author outlines the ways in which drying processes influence the finishing of leather and the effect of binder penetration on grain strength. **II.** *Ibid.*, **130**, 53 (1958).—Polyacrylate and butadiene hydrosol binders, silicone resins, and casein-albumin and nitrocellulose finishes are discussed in detail. J.J.

Tannage and Finishing of Buffed Upper Leather. H. Loewe. *Leather Trades Rev.*, **130**, 433, 469 (1958).—The production of buffed upper leather requires increased firmness and fullness of the grain of chrome-tanned leather so that finishes can be applied that will provide good cementing of fibers and impart a natural appearance to the leather. Firmness and fullness of the grain of the chrome-tanned leather can be achieved by retanning with natural or synthetic tannins and also by resin tannins. The methods of this retannage are thoroughly described. Outlined are several methods of fatliquoring and other operations for preparing the leathers for the finishing operations. The requirements for good finishing of the leather are also given. J.J.

Discussion of Beamhouse Procedure. R. E. Davis. *Leather Mfr.*, **75**, No. 5, 30 (1958).—A discussion of the effects of slow and fast unhairing in terms of merits and disadvantages of each type. J.J.

The "Tanning" and "Detanning" Action of Dyes. G. Otto. *Das Leder*, **9**, 202–9 (1958).—Dyes can have a decided influence on the feel and grain character of chrome upper leather. The effect of a given dye in different tanneries, however, is not consistent. Overneutralization by the dye has been thought to be the cause of poor leather, but equally good leather has been made after doubling the amount of soda that was used to improve the solubility of a substantive dye. Some alkali-free dyes are not as good as some that contain sodium. The action of dyes must therefore be sought in their chemical structure. Anionic dyes of higher molecular weight might be expected to have a tanning action because they do not differ greatly in structure from syntans. Both have molecules made up of several aromatic rings and made soluble by sulfonic acid groups. A comparison was made of the action of a syntan and 3 dyes on limed hide and on chrome leather; all the dyes had tanning action. Diamine-echtbraun GB tanned as rapidly as the syntan. The affinities of the dyes for chrome leather increased with increase in the length of the chain of conjugate double bonds in the dye. The effect of 10 different dyes on the grain bursting strength of chrome skivers was investigated. Dyes of lower molecular weight and which were able to dissolve freshly precipitated, dialyzed chromic hydroxide, increased the bursting strength of skivers tanned without masking, probably because they dissolved excess chrome from the surface layer and distributed it more evenly through the leather. Skivers neutralized with a masking salt, however, had a lower bursting strength after dyeing because too much chrome was removed from the grain layer. Other dyes which could enter the chrome complex

lowered the strength of unmasked but increased that of masked leathers. It is evident that dyes have two different effects and that these may overlap. One action is similar to that of a syntan or vegetable tannin and is found with many dyes having a molecular weight of over 450. These dyes improve leather quality provided the grain is not overtanned and the absorptivity of the leather is not increased so much that finishing is difficult. Brown, green, blue, or black dyes usually must have so many chromophore groups that they tend not only to unite to peptide groups of the skin by hydrogen bonds but also to react with metal atoms of a mineral tannage. Such dyes act as very astringent retanning agents and may overtan the grain if this is not prevented by suitable treatment. The other dye effect is a dissolving of deposited chrome compounds by anionic dyes of small molecular size. In a mixture of dyes the two effects may partially or wholly counterbalance. The effect of masking salts on the absorption of 4 dyes by freshly precipitated chromium hydroxide was tested by treating the hydroxide (*a*) first with a masking agent, then with dye, or (*b*) treating first with dye, then with masking salt. Formate, a weak masking agent, did not prevent take-up of dye and did not displace dye from dyed chromium hydroxide. The strong masking agents, phthalate, oxalate, and hexametaphosphate, prevented take-up of the dyes or displaced them from dyed hydroxide. Citrate, adipate, malonate, and sulfophthalate were intermediate in action. The unfavorable action of dyes on chrome leather can be prevented by use, preferably during neutralization, of a complex-forming salt with medium affinity for chromium. Unfavorable effects of a detanning action by a dye can also be avoided by the use of about 60% basic aluminum chloride either at the end of the tanning process or during fixation of the dye. I.D.C.

The Cause of Yellowing Phenomena on White Leather. E. Quendt. *Das Leder*, **9**, 241–46 (1958).—There are two types of yellowing of white leather, one caused by either sun or ultraviolet light and the other not caused by light. Usually if aniline-dyed or retan (vegetable or syntan) leather darkens or yellows in strong light, the tannin is blamed unless a light-stable material was used, in which case the fat is blamed; fats with a high proportion of unsaturated fatty acids are commonly thought to cause yellowing. In a test with chrome leather that had been milled with 4% of TiO_2 and flour, then oiled with 3% of various oil mixtures, none of the specimens discolored in sunlight (sunlight is better than ultraviolet light for this test). Portions of this leather were then retanned with 4% of 7 different materials and oiled as before. The leather retanned with Tanigan supra LH, Tanigan extra Q, and quebracho discolored greatly; that retanned with a 50-50 wattle-chestnut mixture yellowed moderately; and that with Basyntan supra DLX, slightly. There were only minor differences between the oils, and in every instance the unoiled leather discolored more than the oiled leather. Pigment finishes will completely prevent this type of discoloration. Irreversible color changes, not caused by light, are caused by colored substances that are dissolved from the leather by the solvent or plasticizer of the finishing material either during or after finishing. In some cases yellow-brown flecks on the grain may have been caused by stacking the skins flesh to grain, thus allowing unfixed retanning material or fat on the flesh to transfer to the grain. A relatively new, reversible yellowing was first noticed on shoes stored for a long time in cartons. When the shoes were removed and exposed to sunlight or UV light, the discoloration soon disappeared; but it returned if the shoes were again stored in the dark. This coloring

and bleaching cycle could be repeated several times before it no longer occurred. That this stain was not caused by the leather was established by using leather from a lot that stained in shoes and treating it with various solvents in liquid and vapor form and with different fats; no stains were formed. Fat dissolved from the leather could not be made to produce stains of the type being investigated. This stain, in the form of golden-yellow spots, was caused by a yellow, light-unstable component of Neoprene AC which is used in certain new products marketed as self-vulcanizing cements. Such a component was recovered chromatographically but has not yet been identified. This material diffused through the leather to the grain, and the time required for formation of spots depended on the thickness and type of leather. Some leathers may contain groups that will combine with the yellow material, so that yellow spots will not appear on the surface until all such groups within the leather have been saturated. In general there was very little or no influence on formation of these spots by the solvent or other components of the cement, by type of chrome tannage, or by the components, such as pigments, plasticizers, or solvent, of the finishing material. A rapid test for this type of staining could be made in 1–2 hours by splitting the leather to a thickness of 0.5–1.0 mm., applying test material to the flesh side, and warming it with an infrared lamp. The view of Zoller that the yellow spots are caused by TiO_2-catalyzed oxidation of unsaturated fats and that the yellow, oxidized fat is decomposed by light is not supported by this work. I.D.C.

The Dependence of Leather Quality on its Method of Manufacture, Investigated on Sheep Leather. G. Havas and A. Minculescu. *Das Leder*, **9**, 274–78 (1958).—To find the best tanning conditions for sheepskins a large number of tests were made using 10 left sides for each experimental tannage and the corresponding right sides for a standard method with a glucose-reduced liquor. Each test was repeated with 10 more skins, using the right side for the experimental tannage. The skins were poor-quality Romanian wool sheepskins from animals 18–20 months old. In liming, the length of time and the degree of swelling were decisive; too long a time or too much swelling lowered leather quality. Swelling could be decreased by use of $CaCl_2$ in the limes, but the leather did not finish well if too much (over 0.5%) was used. For pickling, Na_2SO_4 was better than NaCl, and HCO_2H was better than H_2SO_4. The classical 2-bath chrome tanning process was better than a combination 1- and 2-bath process. A combined sulfur chrome tannage was of no value. Masking with up to 1–2 mols of formate or 0.25 mols of lactate per mol of Cr_2O_3 made good leather. Phthalate formed high-molecular chrome aggregates, and distribution of chrome was uneven; however, phthalate-masked liquors made leather with tight grain and full flanks. Improved leather was made by fatliquoring with glyptal resin provided the resin was emulsified properly so it would penetrate. Evaluation of the results of the above tests led to the following process: Soak 24 hr. and set out after 8 hr. Lime with either (*a*) sulfide paste without lime, followed by a lime liquor, containing 5 g. Na_2S (60%) per l., or (*b*) lime-sulfide paste followed by a lime liquor containing sulfide and $CaCl_2$. Degrease with trichloroethylene and a nonionic emulsifier. Tan by one of the three following methods: (*a*) Pickle with HCO_2H and Na_2SO_4, tan with 1.5% Cr_2O_3 having the first portion 35% and the second 45% basic, neutralize with 0.2% $NaHCO_3$ in 20 volumes of water; (*b*) neutralize with $(NH_4)_2SO_4$, dry to 15% moisture, then tan with 1.5% Cr_2O_3 at basicity 35–38%, do not neu-

tralize; or (*c*) pickle to pH 5.5–5.7, tan with a formate- or lactate-masked chrome liquor, and at the end mask further with phthalate. Fatliquor with glyptal resin emulsified with sulfonated mineral oil. Vegetable retan with 2% (pure tannin basis) sumac (*Rhus cotinus*) extract. Before drying, oil the grain with train oil. This type of leather had a strength of 270 kg. per cm^2, a grain strength of 210 kg., and water absorption in 2 hr. of 52% and in 24 hr. of 90%. I.D.C.

Studies on Collagen. II. Properties of Purified Collagenase and Its Inhibition. S. Seifter, P. Gallop, L. Klein, and E. Meilman. *J. Biol. Chem.*, **234,** 285–93 (1959).—A description is given of a method of purifying collagenase which makes possible large-scale preparation of the enzyme. The purification employs $(NH_4)_2\ SO_4$ fractionation, adsorption to alumina gel, and desorption with 0.2*M* sodium phosphate buffer. From sedimentation and diffusion constant data the molecular weight of the purified enzyme was calculated to be 109,000. Organic solvent titrations, formal titration, and ninhydrin reaction indicated that digestion by collagenase of ichthyocol, soluble calfskin collagen, or gelatins derived therefrom, resulted in a degradation product of average molecular weight of 500. About 30 of the peptides can be resolved by two-dimensional paper chromatography. Purified collagenase, free of detectable peptidases and non-specific proteinases, acts only on collagens and gelatins and is shown to be inactive against a number of synthetic compounds. The enzyme is inhibited by sulfhydryl-containing agents, and inhibition by cysteine is not reversed on dialysis. Collagen and gelatin appear to bind collagenase equally; however, gelatin is degraded at a rate approx. 10 times greater than that for collagen. These findings are discussed in relation to the stability of peptide bonds in native and denatured proteins. J.M.C.

Water Ends Pigment Finish Sahara. H. L. Keiner. *Leather & Shoes.*, **136,** No. 7, 18 (1958).—The author states that ruthless removal of water and the destruction of moisture-starved hair cells have an adverse effect on pigmented coated finishes. Modern finishes demand that enough water be added to give good penetration, spread, and level covering. Penetration causes the film to form under the surface as well as on top of the leather. The importance of a protective base coat with nitrocellulose lacquer is mentioned. Formulas are given for the ratio of water to pigment when used on full-grain waist belt, wallet, and side leathers, in split finishing, and on sheepskin. J.J.

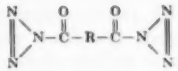
Substitution Reactions of Oxalato-Complex Ions. I. Oxalate Exchange Reactions of the Tris-oxalato-cobalt (III) and Chromium (III) Complex Ions. F. D. Graziano and G. M. Harris. *J. Phys. Chem.*, **63,** 330–33 (1959).—The $[Cr(C_2O_4)_3]^{3-}$ complex is extremely stable at pH 4 to 6, even at 85°C. At lower pH values some $(C_2O_4)^{2-}$ is split off, and at higher pH values a more complicated decomposition takes place, with eventual precipitation of $Cr(OH)_3$. Nevertheless, rapid exchange takes place between free oxalate ions in solution and oxalate ions in the complex. This interchange was studied by the use of oxalate ions tagged with C-14. The kinetics of the exchange reaction were studied, and a possible mechanism is suggested. H.B.M.

Combination of Skin with Acids and Bases. I. J. P. Danby. *Leather Trades Rev.*, **129,** 505 (1958).—A review. J.J.

PATENTS

Coated Leather Products and Methods for Producing Them. U. S. Pat. 2,879,178. Paul W. McWherter, Abington, Benjamin B. Kine, Tullytown, and Hugo A. Alps, Southampton, Pa., assignors to Rohm & Haas Company, Philadelphia, Pa., a corporation of Delaware. Appl. June 29, 1956.—9. As an article of manufacture, a leather having a multi-layer coating thereon, one layer of which comprises a pigmented water-insoluble linear polymer, having an apparent second order transition temperature from −50°C. to −10°C., of about 3 to 15% by weight of dimethylaminoethyl vinyl ether and 97 to 85% respectively of at least one alkyl ester of acrylic acid in which the alkyl group has 1 to 4 carbon atoms, said coating containing 10 to 150% by weight, based on the weight of the polymer, of a pigment, the amount of polymer in the coating being from 1 to 15 pounds per thousand square feet of the leather, and, superimposed on said layer, a pigmented lacquer coating comprising a vinyl resin and a plasticizer for the vinyl resin.

Process for Reacting Protein Fibers with Dicarboxylic Acid Diazides and Products Produced Thereby. U. S. Pat. 2,881,046. William Gordon Rose and Harold P. Lundgren, Berkeley, Calif., assignors to the United States of America as represented by the Secretary of Agriculture. Appl. March 29, 1956.—7. A modified protein fiber comprising a protein fiber having chemically combined therewith about from 0.1 to 25% of its weight of a dicarboxylic acid diazide, produced by reacting said protein fiber with said dicarboxylic acid diazide at a temperature about from 0° to 100°C., said modified protein fiber exhibiting decreased degree of supercontraction, decreased tendency to shrink, and increased resistance of alkalis and acids, said dicarboxylic acid diazide having the formula



wherein R represents a member selected from the group consisting of a direct linkage between the two azide radicals, a saturated aliphatic hydrocarbon radical containing from 1 to 14 carbon atoms inclusive, an unsaturated aliphatic hydrocarbon radical containing from 2 to 5 carbon atoms inclusive, the benzene radical —C_6H_4—, the methylbenzene radical —CH_2—C_6H_4—, the cyclohexane radical —C_6H_{10}—, the radical

—CH_2—O—CH_2—

and the radical —CH_2—O—C_6H_4.

Process of Tanning Hides with Polymethoxyaldehyde Compounds and Optionally Vegetable Tanning. U. S. Pat. 2,880,053. Martin L. Fein, Riverside, N. J., and Edward M. Filachione, Philadelphia, Pa., assignors to the United States of America as represented by the Secretary of Agriculture. Appl. Jan. 3, 1956.—1. The process for tanning hides comprising impreg-

nating the hides with an alkaline solution of a polymethoxyaldehyde having the formula

$$CH_3—(CH—CH_2)_n—CHO$$
$$\quad\quad\quad

Leather-rolling Machines. Brit. Pat. 809,179. Maschinenfabrik Moenus A.G. Appl. Feb. 18, 1957.—In a machine for smoothing leather, wherein a

FIG. 1.

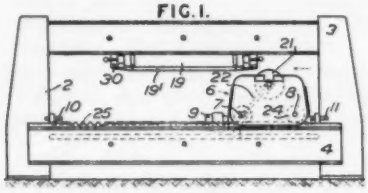


FIG. 3.

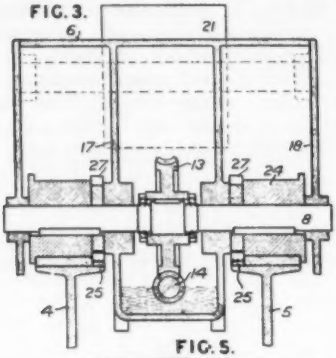
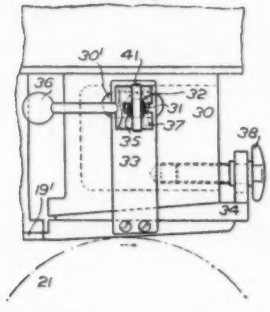


FIG. 5.



carriage bearing a revoluble and upwardly-pressed pressure roller is moved to and fro on rails to press the leather against a pressure plate, the carriage is self-propelled by a power unit thereon driving its running wheels. Uprights 2, 3 of the machine frame carry two rails 4, 5 on each of which run two wheels 24 of the carriage 6. The wheels 24 are keyed to axles 7, 8 which are journalled in bearings in intermediate and end walls 17, 18 of the carriage. Also keyed to the axle 8 are pinions 27, Fig. 3, which engage racks 25 fitted to the rails 4, 5, and a worm wheel 13. A worm 14 engages the worm wheel 13 and is driven by an electric motor 9 mounted on the carriage, thus causing the

axle 8, wheels 24 and pinions 27 to rotate and the carriage to move along the rails 4, 5. Abutments 10, 11 at each end of the rails operate reversing switches so that the carriage moves to and fro between them. The pressure roller 21 is spring mounted in the top of the carriage 6 and is driven, e.g. by a bevel gear arrangement 22, from the axle 7, in the opposite direction to the wheels 24. The leather is held against the underside of the pressure plate 19^1 of a heated pressure chest 19, which is covered by a sheet of felt or leather, by a table not shown in the drawing, and is embossed by the roller 21 which presses up against it. Ramps 30 are disposed at each end of the pressure chest 19 to avoid shock when the roller 21 runs on to the leather on the pressure plate 19^1. Each ramp 30 has a shoe 34, Fig. 5, attached to two plates 33 which depend from the eccentric end portions 32 of a shaft 31 journalled in slots 30^1 in the ramp walls. The shaft 31 has a flat extension 35 at one end to which a handle 36 having a forked part 37 is pivoted by means of a pin 41 so that by swinging the handle on its pivot away from the machine the forked part 37 presses on the adjacent plate 33 and both plates are drawn toward each other and clamped against the walls of the ramp 30 when the handle 36 is at a right angle thereto. To accommodate varying thicknesses of pressure plate the shoe 34 is raised or lowered by the eccentrics 32 when the handle 36 is turned and a wedge is slidable laterally, by means of a screw 38, between the shoe and the body of the ramp so that no gap is left therebetween. The shoe 34 is also adjustable laterally by moving the shaft 31 along the slots 30^1. Dished springs threaded on bolts may be used to support the roller 21 (*see* Group XXXII), the lower springs being thinner than the upper ones so that the first pressure is gentle and yielding.

Water-proofing Leather. Brit. Pat. 806,093. Rohm & Haas Co. Appl. June 1, 1956.—Compounds of the formula

$$CH_2{=}CR^1{-}CO{-}X{-}A{-}NH{-}CO{-}NH{-}R$$

where A is an alkylene group of 2–4 carbon atoms, R is a *t*-alkyl group of 12–18 carbon atoms, R^1 is H or methyl and X is —O— or —NH—, and useful for softening, lubricating and imparting water-repellency to substrates such as leather. In an example N-β-methacryloxyethyl-N^1-*t*-alkylurea (a soft solid if the alkyl group has 18–24 carbon atoms—mainly C_{18} in the example) is rubbed on leather to make it water-repellent and more flexible. The compounds may also be added in the fatliquoring operation.

Flexible Leather. Brit. Pat. 808,257. Plot, J. Appl. April 18, 1957.

Flexible leather, particularly suede leather, for use in shoe uppers or articles of clothing, wherein the reverse face of the leather is provided with a plurality of uniformly distributed fine holes which extend for a predetermined depth of the leather but terminate short of the obverse face of the leather so that said obverse face remains unaltered. The holes are preferably conical in shape

and their depth is ⅓–⅔ of the thickness of the leather. There may be 6–15, preferably 9–10, holes per sq. cm. The depth of the hole may be 1.8 mm. and its diameter at the face 1.0–1.2 mm. Fig. 2 is a fragmentary sectional view through a sheet of leather which has been treated with a tool shown in fragmentary sectional view in Fig. 4.

Tanning and Shaping Leather. Brit. Pat. 807,741. Secotan Inc. Appl. Oct. 11, 1956.—Skins are tanned, dehydrated and may be moulded and fat-liquored in a process where the untanned skin is treated with an aqueous solution of an inorganic or mineral tanning agent, such as chrome, iron, titanium or zirconium, which is preferably heated to 20°F. below the shrinkage temperature of the skin, and the treated skin is subsequently dehydrated and may be moulded to form hollow leather articles such as shoe uppers, by fluid pressure on the skin supported on the surface of a porous material such as plaster of Paris or wool felt. The dehydration is conducted by forcing an inert water-miscible organic solvent, e.g. acetone, from skin to mould surface. The tanning agent is fixed to the skin by neutralization either before the water extraction process by an aqueous solution of a base, or during extraction or after extraction by a base which may be forced in non-aqueous solution or mixed with a fat-liquoring solution through the skin while it is still supported on the porous surface. The fat-liquoring solution which may be employed comprises a fatty acid, e.g. stearic acid, dissolved in a water-miscible organic solvent. Finally the skin is dried of solvent to render it completely and permanently tanned. In examples the production of moulded shoe uppers from untanned skin is described. Specifications 726,777, 726,828 and 755,969 are referred to.

Precipitation of Tannins and/or Proteinaceous Substances from Liquid Media. U. S. Pat. 2,875,062. Jesse Werner, Holliswood, N. Y., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware. Appl. Oct. 31, 1957.—1. The process of precipitating substances selected from the group consisting of natural tannins and protein-tannin complexes from liquid media containing the same which comprises adding to the said liquid media, in a precipitating amount, a polyvinylimidazole having a molecular weight of 20,000 to 400,000 and removing the precipitate from the liquid media.

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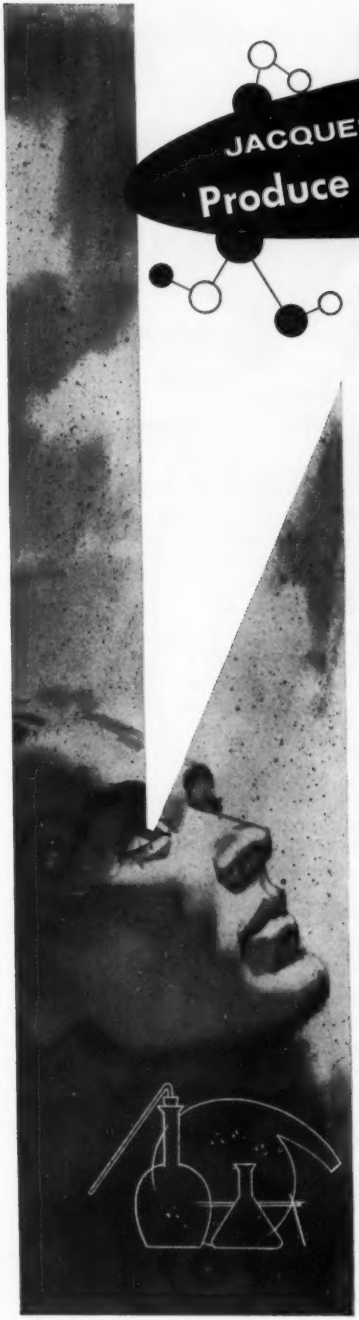

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LIQUID (25% Cr_2O_3)

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INDEX TO ADVERTISERS

ADOLF SCHUBERT XXXII
ALLIED CHEMICAL CORP., Solvay Process Division ..... IX—XXVII
APEX CHEMICAL CO., INC. XXXI
ARKANSAS COMPANY, INC. XXVI
AMERICAN CYANAMID COMPANY, Dyestuff Department XV
ARTHUR C. TRASK CO. VII
ARTHUR THOMAS CO. XXII
ATLAS REFINERY XI
BARKEY IMPORTING CO., THE XIX
BAY STATE OIL PRODUCTS XXX
BJORKSTEN RESEARCH LABORATORIES XXX
BONA ALLEN, INC. XXXIII
BORNE CHEMICAL CO., INC. XVIII
CHEMICAL COATING MATERIALS CO. XX
CHEMTAN COMPANY ..... Outside Back Cover
COMET CHEMICAL CO., INC. XXXIII
COMMONWEALTH LABORATORIES, INC. XXVIII
EASTERN INDUSTRIAL OIL PRODUCTS CO. XXIX
E. F. DREW & CO., INC. XXXIII
EISENDRATH TANNING CO. XXX
FIBER CHEMICAL CORPORATION XXXVII
GARDEN STATE TANNING, INC. XXXIV
GEIGY COMPANY, INC. VIII
HOOKER CHEMICAL CORP. III
HOWES LEATHER CO., INC. XXXIII
INTERNATIONAL PRODUCTS CORPORATION XIII
JOHNSON AND CARLSON XXXVII
KEPEC CHEMICAL CORPORATION XXXIV
LEATHER AND SHOES XXIV
LEATHER MANUFACTURER, THE XXXI
L. H. HAMEL LEATHER CO. XXXIII
L. H. LINCOLN & SON, INC. V
MARDEN WILD CORPORATION XXXV
MARSHALL LABORATORY XXXV
MOBIL OIL CO., INC. XXI
NEWARK LEATHER FINISH CO. XXXVI
NOPCO CHEMICAL CO. XXIII
OHIO LEATHER CO., THE XXX
OLSON IMPORTING COMPANY, INC., THE ..... Inside Front Cover
PRESTO COLOR CO. XXXIV
PRIME LEATHER FINISHES CO. XXXII
PROCTOR AND SCHWARTZ, INC. XXIX
REILLY-WHITEMAN-WALTON CO. XXXII
ROBESON PROCESS CO. II
ROHM & HAAS IV
SALEM OIL & GREASE CO. XXVIII
SAXE CUTCH CORPORATION XXXII
SEABOARD CHEMICALS, INC. ..... Inside Back Cover
TANIMEX CORPORATION ..... X—XIV
TANNADE COMPANY XXXVII
TANNER'S COUNCIL RESEARCH LABORATORY ..... XXXIV—XXXVI
TANNINS & CHEMICALS, INC. VI
WALLERSTEIN COMPANY, INC. XVII
WARNER CO. XXXV
WEBER & SMITH, INC. XXXIV
WHITTEMORE-WRIGHT CO. XXXVI
WOLF, JACQUES & CO. XXV
YOUNG CO., J. S. ..... XII—XVI

New Esterified Oils Offer Major Benefits To White Tanners

An important development was announced recently by a leading manufacturer of tanning chemicals.

After considerable basic research, Seaboard Chemicals, Inc. is the first to offer the tanner a new concept in white leather fatliquors. It's a series of esterified oils called the Polarsols.

Tannery production runs indicate that these oils possess an attractive combination of properties that can help white tanners get more top-grade leather per pack and those already using the Polarsols claim the temper of their stock can be kept under absolute control, from mellow all the way to super-soft.

Unlike ordinary sulfated oils, which tend to produce looser leather as oil percentage increases, Seaboard's new esterified oils produce an overall tight break regardless of oil percentage used. Reports from the field indicate this is true even out into the flank and belly areas, with the result that an unexpected bonus of additional high-grade leather can be produced. And there is less trimming when the stock is finished.

To check oxidation characteristics, rigid Fadeometer tests have been conducted over a period of time on various types of leathers fatliquored with the Polarsols. These bleached esterified oils proved to be unusually light fast, easily passing 120-hour specifications. Also the Polarsols showed excellent stability where residual alum was present.

Perhaps one of the most attractive characteristics of these new esterified oils is the amount of money they save. According to Seaboard, the Polarsols soften leather to a greater degree than sulfated oils, so significant savings can be expected. Field experience has borne this out, with many tanners reporting they can get the same degree of softness in their stock with 20% less oil.

There is a Polarsol for every type of white leather—whether it be sides or splits, suedes or grains, kid or calf. The manufacturer offers percentage suggestions for use. To get detailed information and a trial sample of one of the Polarsols, specify your type of leather. Write or phone Seaboard Chemicals, Inc., Dept. 7G, 30 Foster St., Salem, Massachusetts, U. S. A. In Canada: Tennant Union, Ltd., Toronto and Montreal.

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